Doctoral Thesis

Study of mechanisms and efficiencies of electrochemical lithium recycling system

Hyuntae Bae

School of Energy and Chemical Engineering

(Battery Science and Engineering)

Ulsan National Institute of Science and Technology

2021

Study of mechanisms and efficiencies of electrochemical lithium recycling system

Hyuntae Bae

School of Energy and Chemical Engineering

(Battery Science and Engineering)

Ulsan National Institute of Science and Technology

Study of mechanisms and efficiencies of electrochemical lithium recycling system

A thesis/dissertation submitted to
Ulsan National Institute of Science and Technology
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Hyuntae Bae

Month/Day/Year of submission

Approved by

Advisor

Youngsik Kim

Study of mechanisms and efficiencies of electrochemical lithium recycling system

Hyuntae Bae

This certifies that the thesis/dissertation of Hyuntae Bae is approved.

06.09.2021 of submission

Signature

Advisor: Youngsik Kim

Signature

Seok Ju Kang

Signature

Dong Woog Lee

Signature

Kyung Hwa Cho

Signature

Shun Myung Shin

Signature

Abstract

As the lithium-ion battery (LIB) has been widely commercialized for energy storage systems in portable and stationary devices, its production and disposal have dramatically increased over the past few decades. In addition, increasing amounts of electric vehicles (EVs) and energy storage systems (ESSs) causes a dramatic increase in waste LIBs. As lithium is the key material for LIB, this increasing market trend of LIB leads to lithium depletion which is an urgent problem for the future LIB market.

To circumvent these issues, various LIB recycling technologies have been researched. However, the conventional lithium recycling methods have a problems of using toxic and high-cost acid chemicals to leach the waste battery materials and consume high energy to increase the temperature by over 100 ℃. This leads to complicate the procedure and requires environmental treatment processes and costs.

A new type of lithium recycling system has been proposed to overcome these issues. This electrochemical system is named the waste-to-lithium (WTL) recycling system and can simply extract lithium from the waste lithium materials. By electrochemically charging the WTL system, lithium ions from the waste LIB materials are extracted and pass through the lithium ion conducting solid electrolyte to form lithium ion in the anode compartment of the WTL system. After the charging process, by electrochemically discharging the system, extracted lithium can be transformed into Li_2CO_3.

The concept of the WTL system is proved with pre-treated waste powders from waste LIB. The electrochemical charging and discharging mechanism for WTL were investigated based on the reaction potential difference of OER/ORR, which is dependent on the pH of the solution. And the lithium extraction efficiency showed 82.2 %. For the increasement of the efficiency, the resistance of each component was investigated with impedance spectroscopy.

This WTL system needs no additional chemicals and operates at room temperature, which can be a promising system for the low-cost and eco-friendly lithium recycling system for the sustainable future energy market.

Contents

List of Figures

List of Tables

1. Introduction

1.1. Importance of Lithium

There has been growing interest in lithium. Lithium consumption has been increasing Lithium consumption has more than doubled over the last decade. **(Figure 1)** [1,2] In 2011, 30% of the lithium usage was for ceramics and glass, followed by batteries and grease/castings. [3,4] However, the application of batteries expanded to small electronics such as smartphones, laptops, as well as larger systems such as electric vehicles (EV) and energy storage systems (ESS), which led to 60% of lithium being used for batteries. **(Figure 2)** [5] Lithium is preferred as the material for batteries due to its three properties: (1) It is the lightest of all metals, (2) has the highest electrochemical potential, and (3) has the highest energy density. [6] In addition to batteries, lithium is also applied in various areas such as ceramics, glass and grease/castings with certain chemical properties. Adding lithium in ceramics increases the glass melt rate and decreases its viscosity and melt temperature. Additionally, the high thermal expansion coefficient of lithium makes it more resilient to heat shocks and increases mechanical strength. [7] Lithium grease is useful in concentrating oil to produce high-temperature grease, [8] and lithium additives are used to casting for adding fluidity. [9] Organic lithium material is used as strong bases in polymers to form carbon-carbon bonds. [10]

Despite lithium's versatile usage, the reserves and production of lithium are not evenly distributed worldwide. 70% of the world's lithium is deposited in South America such as Chile, Bolivia, and Argentina. **(Figure 3)** [11] Australia produces the most lithium (43.5% of worldwide production), followed by Chile (32.8%). [12] Argentina and China export a significant amount of lithium as well. [12]

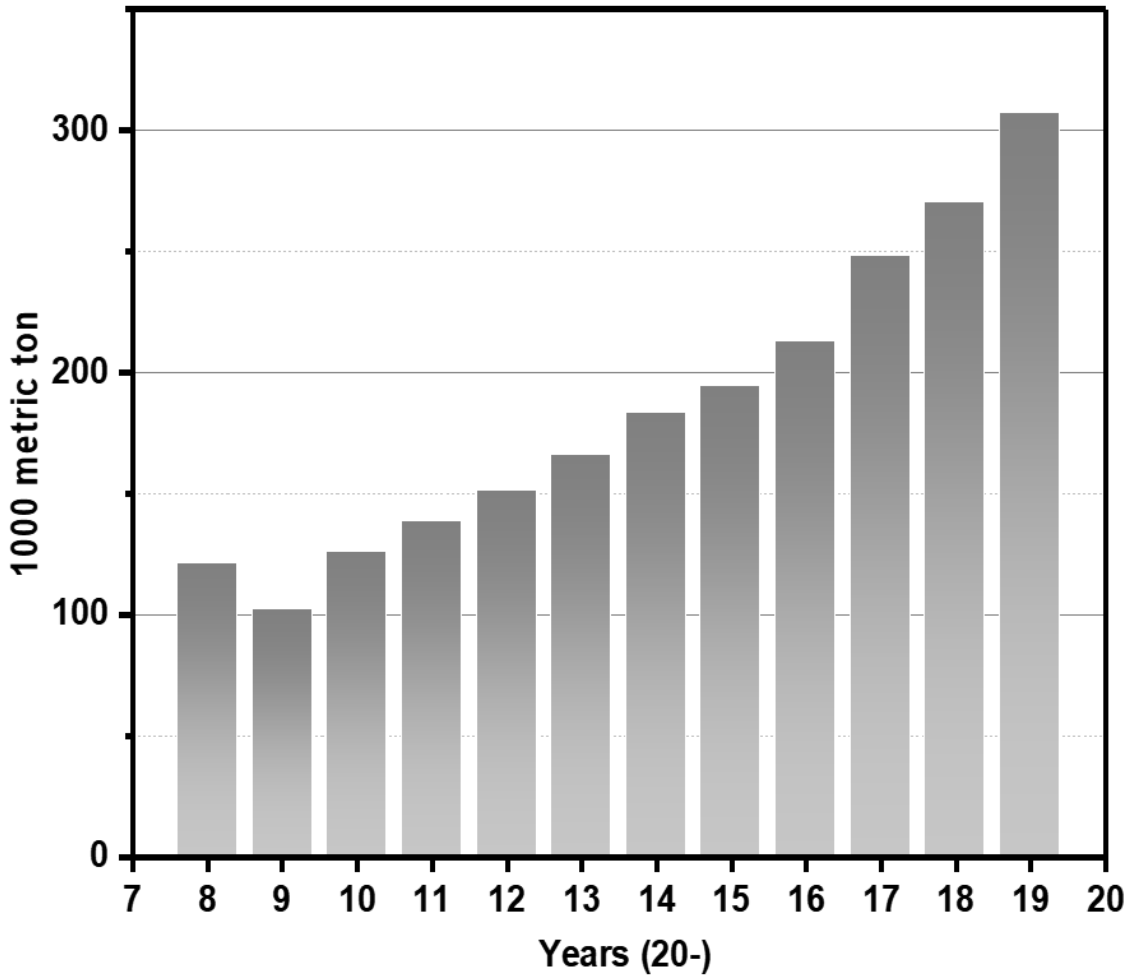


Figure 1. Lithium demand increase

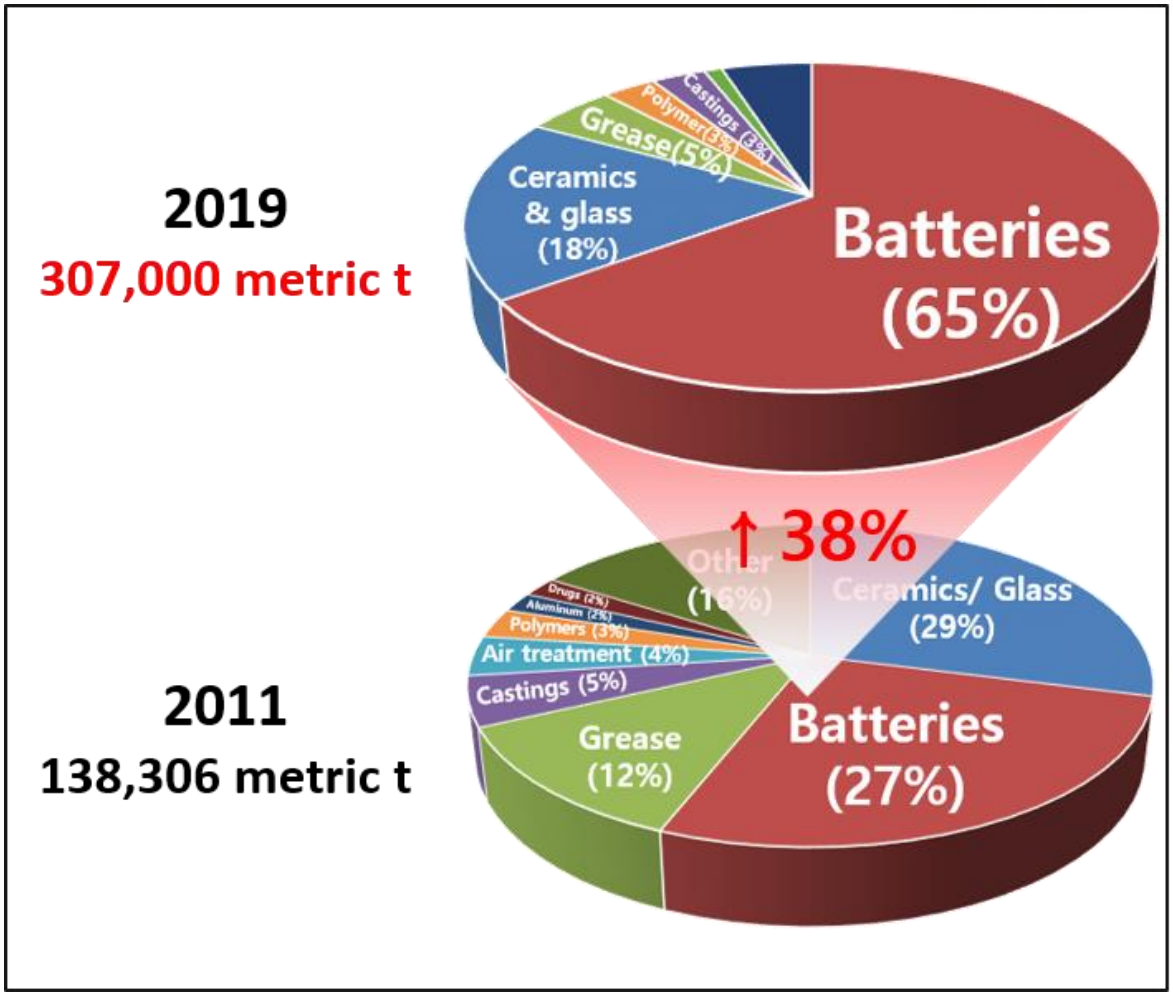


Figure 2. Lithium usages in battery increase

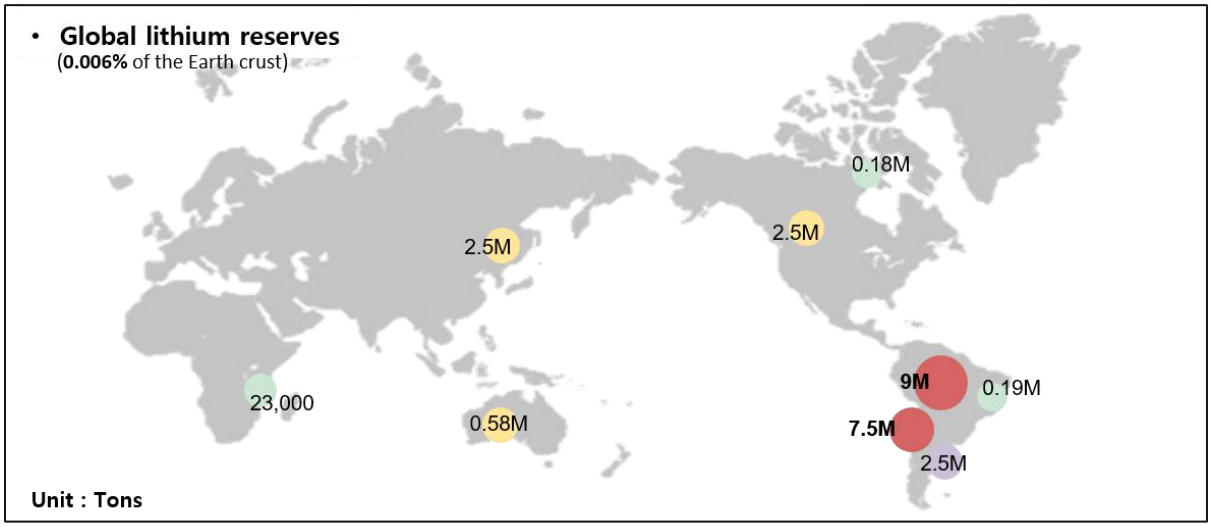


Figure 3. Limited lithium distribution through countries

1.1.1 Extraction of lithium from natural source

Naturally, lithium is extracted from two sources – ores and salt lakes. Lithium can be extracted from spodumene, petalite, and eucryptite, and the composition of lithium ranges between 2 to 5.5%. [13] **(Table 1)** The minerals are crushed, separated by gravity flotation, concentrated, heat processed for water leaching, undergo acid treatment and pressure leaching to produce the lithium solution. Na_2CO_3 is added to the produced lithium solution to extract lithium sediments. [11, 14, 15]

The second method to extract lithium is from a salt-lake or brine. Lithium brines exist in Argentina, Bolivia, Chile, China, and the USA. [14] The lithium grade and the Mg/Li ratio of the brine are important, and these factors affect production cost and time. [16-21] **Table 2** lists the lithium content, Mg/Li ratio of the brines currently used from production. [14] Brine contains 0.02 to 5% Li^+, and also contains other ions such as Na^+, K^+, Cl^-, SO_4^{2-}. [20] Lithium is extracted from the brine using the precipitation method. Water is evaporated from the brine on a solar pond, followed by precipitation of NaCl and KCl, and concentrating lithium in the solution. Next, $Ca(OH)_2$ is added to the concentrated lithium brine to remove Mg and sulfate via precipitation. The Ca and Na_2CO_3 left in the concentrate are removed via precipitation using $CaCO_3$. This fluid then undergoes filtration and washing and heated to 80-90 ℃ to react with Na_2CO_3 to form Li_2CO_3. **(Figure 4)** [20] While solar evaporation followed by precipitation is a widely known method, the procedure is time consuming, lasting 18 to 24 months. [21] For a brine with a high Mg/Li ratio, Al is used to precipitating out lithium-aluminate. This method has a superior lithium separation and precipitation rate. [22] This method adds $AlCl_3$ H_2O, NaOH, and amorphous $Al(OH)_3$, adjusts the temperature and pH to extract lithium as lithium aluminate (Equation 1).

$$LiCl + 2AlCl_3 + 6NaOH \rightarrow LiCl{\cdot}2Al(OH)_3\ H_2O + 6NaCl \quad (1)$$

While extracting lithium from ores have a higher lithium concentration, the production cost is higher than brine extraction due to a more energy intensive procedure. Thus, 87% of the lithium is produced by brine extraction. [23] Lithium also exists in abundant seawater, but the concentration is too low (0.17 ppm) to be economical and the research is ongoing to reduce costs of lithium extraction. [24,25]

Table 1. Various lithium ores and their lithium content

Ore	Chemical Formula	Li contained (wt.%)
Spodumene	$LiAlSi_2O_6$	3.73
Petalite	$LiAlS_{i4}O_{10}$	2.09
Amblygonite	$(Li,Na)AlPO_4(F,OH)$	3.44
Lepidolite	$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$	3.58
Eucryptite	$LiAlSiO_4$	5.51

Table 2. Various lithium salt lakes and lithium content and Mg/Li portion

Salt lake	Country	Li contained (%/ton)	Mg/Li
Atacama	Chile	0.15	6.4
Hombre Muerto	Argentina	0.062-5	1.37
Rincon	Argentina	0.033	8.61
Uyuni	Bolivia	0.035	18.6-21.5
Silver peak	USA	0.023	1.43
Zhabuye salt lake	China	0.12	low
DXC salt lake	China	0.04	0.22

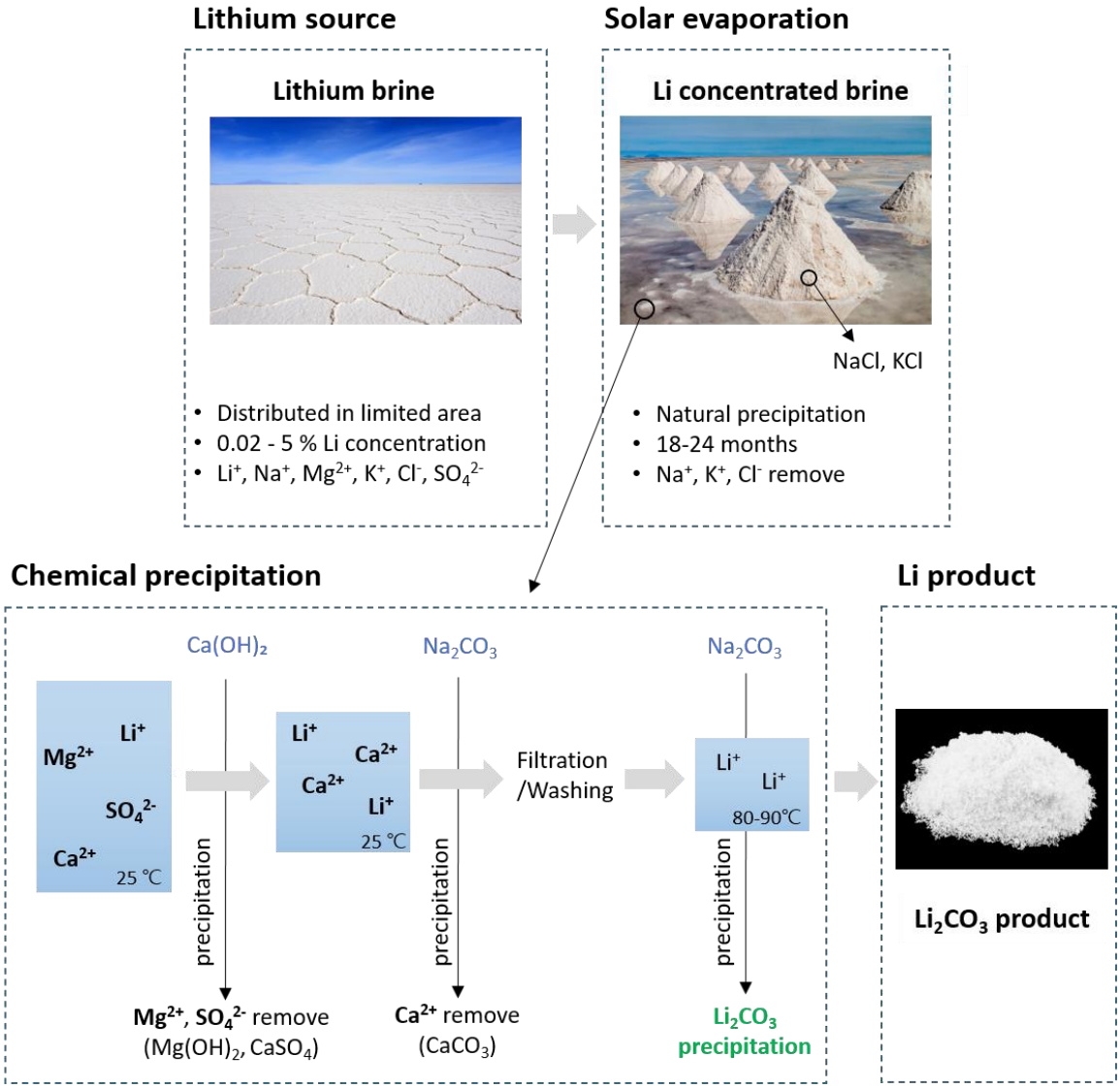


Figure 4. Difficulty of extraction of lithium from natural resources

1.1.2 Current state of lithium

The price of Li_2CO_3, which is commonly traded in the world lithium market, has been increasing, with 2.6 times increase from 2015 to 2018. **(Figure 5)** [26] There is a steady increase in personal electronics (which have lithium batteries), and a significant increase in EVs and ESSs due to the interest in green energy. These trends have expanded the lithium-ion battery market to 40 billion dollars. [27] The growth is accelerating due to the growth in ESS and EV battery markets. To illustrate the potential increase in demand, smartphones, laptops, and tablets contain 2, 6, and 20 grams of lithium, respectively. [28] On the other hand, EV batteries require approximately 20 kilograms of lithium, which is 1,000 times that of smartphones and 10MWh ESS require at least 700 kilograms of lithium. [28,29] As the demand and importance for lithium-ion batteries increase, the price increase of lithium can damage the LIB market.

Lithium consumption has increased from 49,100 tons in 2018 to 57,700 in 2019, an 18% increase. [30] The worldwide lithium reserves are estimated to be 17 billion tons. If the 18% annual increase in consumption continues, the worldwide lithium reserve will be exhausted. In 30 years, the demand for lithium will be approximately 63 million tons, which will be 40 million tons over the remaining reserves. **(Figure 6)** Though there can be more discoveries of lithium reserves, the increase in demand is predicted to accelerate due to the increasing market of lithium-ion batteries. An increasing number of institutions forecast shortages in lithium and the interest in lithium shortages is a world-wide issue. [31,32]

For these reasons, lithium is expected to be valuable in the near future, which highlights the importance of lithium recycling. There is worldwide research on lithium recycling, most of which are focused on recycling lithium from waste lithium-ion batteries.

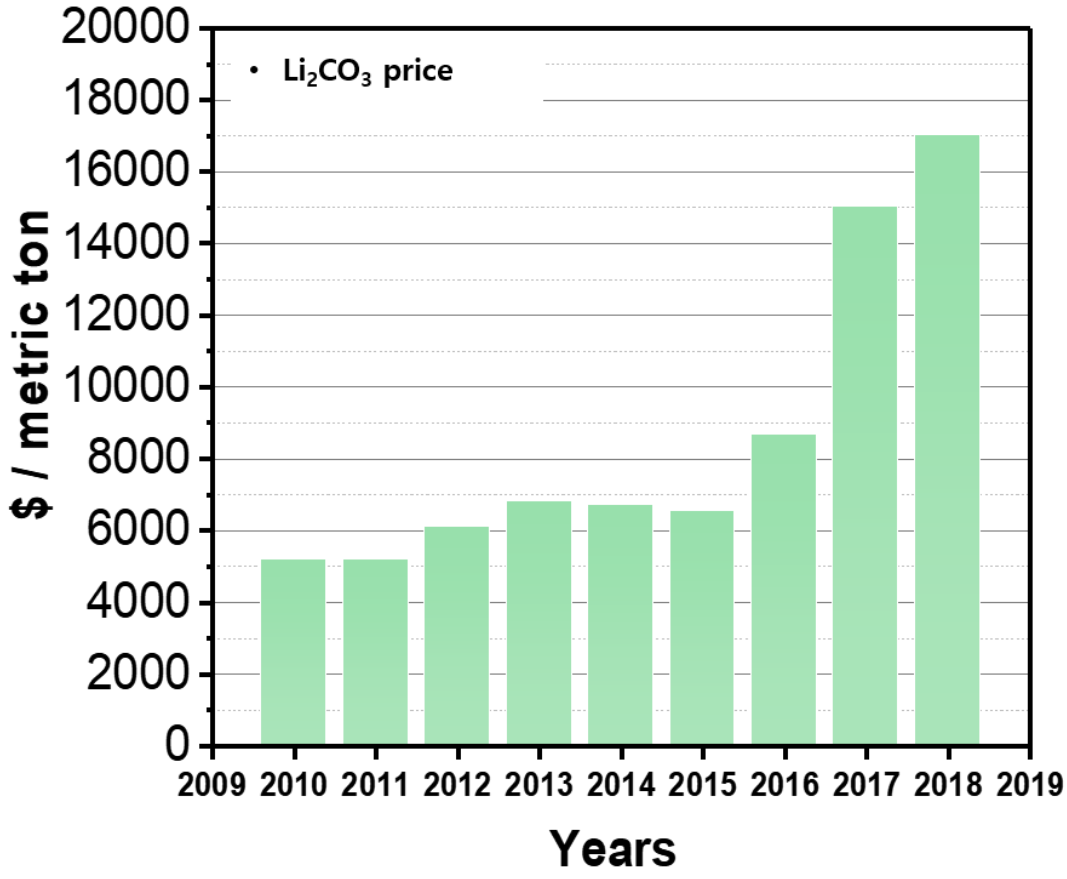


Figure 5. Lithium price increase

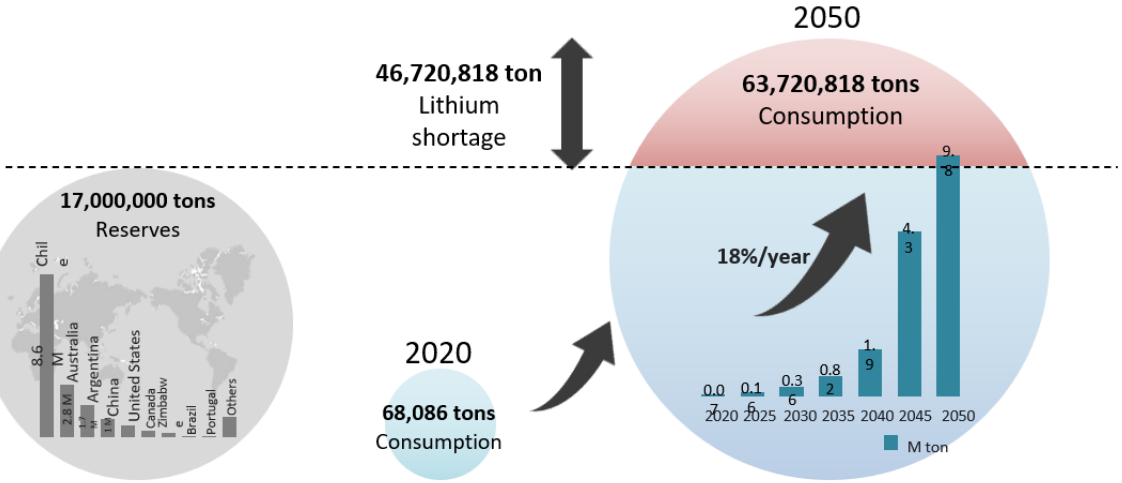


Figure 6. Lithium demand exceed the supply in near future

1.2. Lithium recycling from waste lithium-ion battery

1.2.1. Waste lithium-ion battery collection state

As explained above, lithium recycling research is focused on recycling lithium-ion batteries. Lithium-ion batteries function by moving Li^+ using electrons, and is consisted of an anode, cathode, electrolyte, and a separator. The cathode, depending on the usage and capacity, consists of lithium-containing compounds such as $LiFePO_4$, $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$. The anode consists of carbon material that can accept lithium ions, such as graphite. The cathode and the anode are combined with a polymer binder, such as polyvinylidene fluoride (PVDF), for electric conduction and stability. Electrolytes are usually liquids, and act to deliver the lithium ion between the cathode and the anode. Electrolytes are usually lithium salts (e.g. $LiPF_6$) dissolved in organic solvents, such as ethylene carbonate (EC) or dimethyl carbonate (DMC). Polymers such as polypropylene (PP) or polyethylene (PE) are used for separators, to prevent physical contact and direct electron transfer between the cathode and the anode.

A lithium-ion battery can last up to three years in a small electronic device, and five to ten in a larger device, which is shorter than other batteries, considering Ni-Cd batteries last 15 to 20 years, and lead-acid batteries last 5 to 10 years. Currently, 80% of lithium-ion batteries are used for small electronics, with EV and ESS applications less than 20%. [33] Lithium-ion battery the disposal is estimated to be 10,700 tons in 2012. [34] This value has increased annually, up to 250,000 tons of disposal estimated in 2020. [33] With the large-scale adoption of EVs and ESSs, disposal amount of lithium-ion batteries is expected to increase. The disposed lithium-ion batteries are collected according to the national legislation or producer responsibility institution. Consumers normally dispose the lithium-ion batteries in a government-designated place or are directly collected by a government or producer-led collection institution. Only 2-5% of lithium-ion batteries are collected in Australia, the EU, and the US. **(Figure 7)** [35] The reason for the low collection rate is due to the lack of information by the consumer, as well as consumers keeping their electronics for resale instead of recycling. Although it may vary by country, there is a lack of legal and physical infrastructure for widespread collection, as well as a lack of an efficient way to store and transport the disposed lithium-ion batteries economically. Major improvements will be required to significantly increase the collection rate.

Recycling technology of lithium-ion batteries has been steadily researched since the 1990s and has recently been gaining traction. **(Figure 8)** However, most of the research focuses not on lithium but on more expensive materials such as cobalt. Therefore, very little focus is on primarily extracting lithium from the disposed batteries. Cobalt is the most expensive material in a lithium-ion battery, thus there has been recent interest in reducing cobalt by its content or replacing it altogether, using $LiFePO_4$ or $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$. [36] However, lithium is an irreplaceable, key ingredient in a LIB, used in the

cathode, electrolyte, and anode. Therefore, a comprehensive review of recycling lithium from LIB recycling is needed.

Lithium can be extracted from a lithium-ion battery with two major processes. Due to the difficulty of separating lithium from the packed battery, the disposed battery undergoes a pre-treatment process to separate lithium-containing active material (cathode, anode) from peripheral parts (plastic, polymer). Next, the lithium is chemically separated from the active materials using pyrometallurgy, hydrometallurgy, electrochemical extraction methods. **(Figure 9)** The two major processes, pre-treatment and lithium extraction, will be further explained.

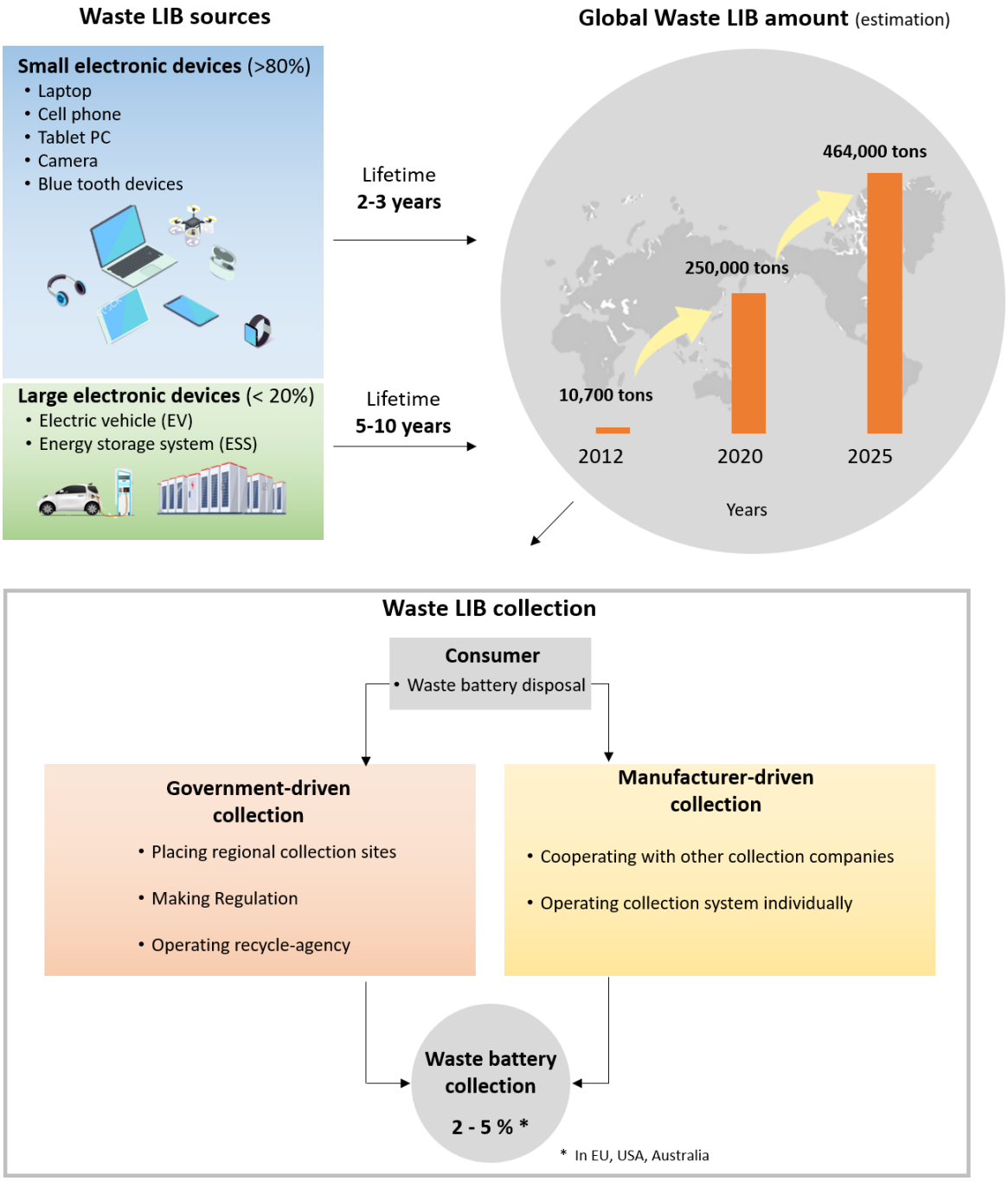


Figure 7. Current state for collecting waste lithium-ion batteries

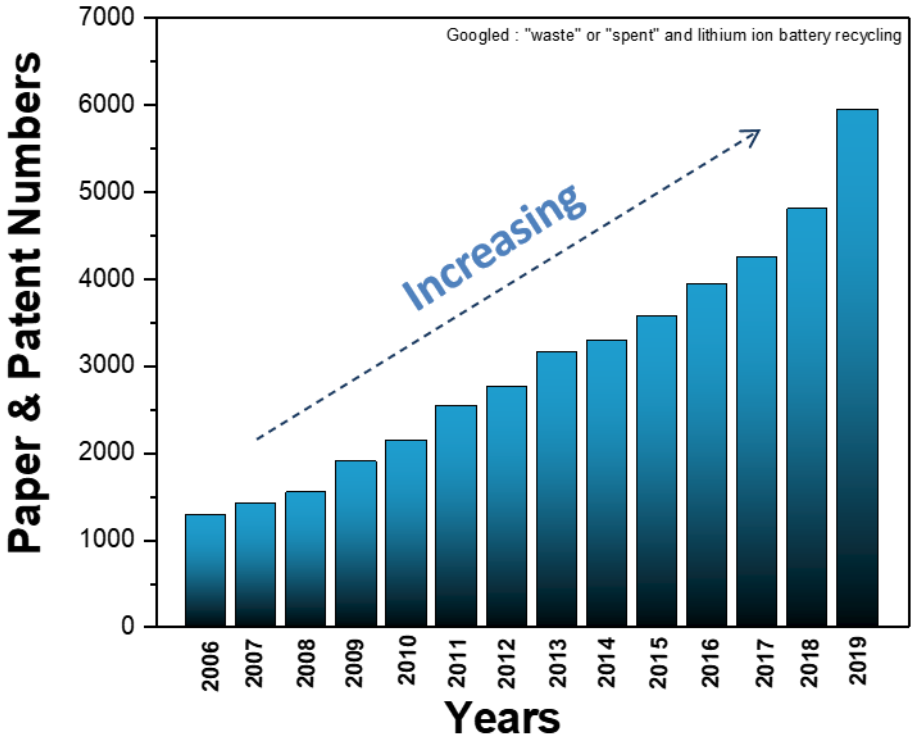


Figure 8. Needs for lithium recycling from batteries

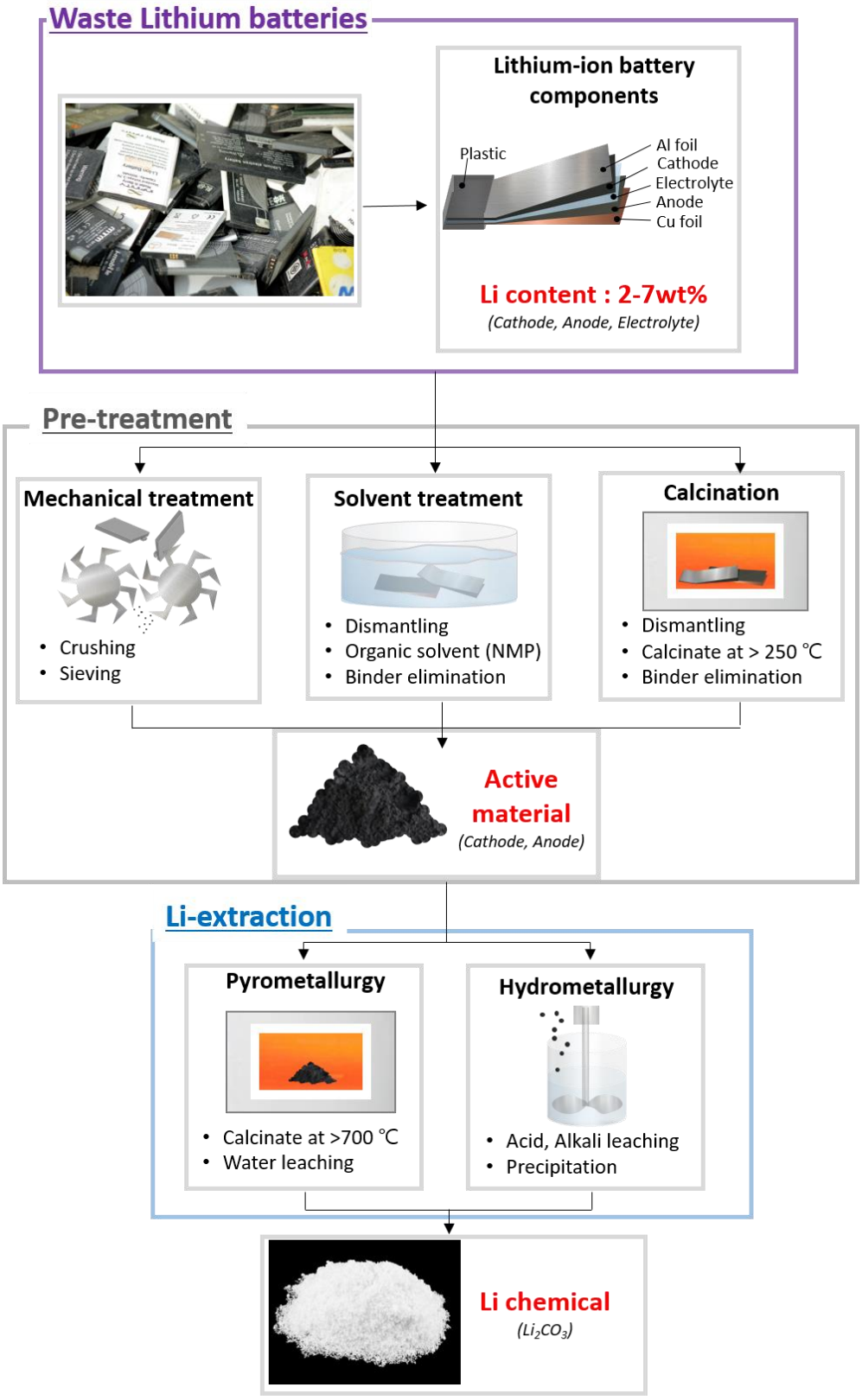


Figure 9. Battery recycling process

1.2.2. Waste lithium-ion battery pre-treatment process

Recent Recognizing the left power of a disposed lithium-ion battery is difficult. After depleting the charge of the battery, the battery might still have some power remained. Also, since lithium-ion batteries contain various materials, it is not efficient to directly treat batteries. Therefore, generally pre-treatment process essential. Waste lithium-ion batteries can be pre-treated and separated safely only when fully discharged. If not, the battery can explode, or emit toxic gas due to a local short circuit. Hauck and Kurrat reviewed various methods to discharge batteries using electronic techniques and conductive liquids. [37] The most common method is submerging the battery in a conductive solution such as a NaCl solution. Although NaCl is the most used conductive solution, there is ongoing research on the discharge rate and corrosion rate of other conductive liquids. [38,39] Methods to separate the active material from the disposed battery can be largely categorized as mechanical separation, solution treatment separation, and calcination treatment separation. **(Figure 10)**

Mechanical pre-treatment

Mechanical pre-treatment is a treatment method to physically grind the discharged lithium-ion battery. **(Figure 10a)** Different compartments of the battery have various mechanical properties, so a grinder that can uniformly grind all the compartments is needed. Generally, a grinding chamber is created with blocking the air. Various tools, such as hammer mills, granulator machines, and blade crushers, are used. After grinding, the active material (cathode, anode) and miscellaneous metal (Al, Cu) are separated using the density and magnetism differences. [40-45] Zhang et al. created battery pieces by shear crushing a waste battery discharged via NaCl solution submersion. [40] They used impact crushing equipment equipped with blade crushers, and ground the battery for 20 seconds with 3000r/min. The crushed pieces were categorized by four groups by size via dry sieving. The larger plastic, Al, Cu, and polymers were separated from the cathode and anode containing 0.075mm materials. After removing the hydrocarbon material on the surface, $LiCoO_2$ and graphite were separated via flotation. Mechanical pre-treatment is the most common method of lithium-ion battery separation due to its simplicity and scalability. However, setting up a stable separation setup is essential, and this method can cause noise, dust, and harmful gases. Also, it is difficult to perfectly separate all the materials using this method.

Solvent pre-treatment

Solvent pre-treatment utilizes solutions and solvents to separate the active materials from the Al, Cu foil from the lithium-ion battery. This method removes the additive binder material that strengthens the foil contact with the active materials, thereby separating the active materials. [46-49] The cathode and anode are combined with a binder on the Al and Cu foil. By removing the binder, the active material can be separated from the metal foil. A well-known method is to insert the electrode plate into an organic solvent (N-methyl-2-pyrrolidine (NMP)) at 100℃ to remove the binder, and to separate the Al, Cu foil. L-P. He et al. discharged the lithium-ion battery by submersing to NaCl solution and separated the battery by hand using sharp nose pilers. [48] After separating the plastic, metal case, electrode plate and separator, the cathode was cut into small pieces. The pieces of the cathode are put in NMP at 80℃ for 2 hours, thereby dissolving the binder, and separating the Al foil and cathode material. **(Figure 10b)** Most batteries use the PVDF binder to attach active materials, but as the batteries are diverse, some use PTFE binders, which require a selection of an appropriate organic solvent. Also, this method uses organic solvents at 100℃, which is costly and creates harmful waste products.

Calcination pre-treatment

Calcination pre-treatment uses heat to remove the polymer and carbon materials from the electrode plate. The treatment occurs at the temperature of 150℃ to 500℃ to remove carbon and organic material from the waste LIB. Also, by calcination at 250℃ to 350℃, the PVDF binder (which connects the active materials and metal foil) can be removed, thereby reducing the adherence of the active materials from the Al, Cu foils. [50-53] Yang et al. cut the cathode parts into small pieces and put them in a nitrogen-condition tube furnace at 550℃ to 650℃ temperature. Then the cathode and the current collector (Al foil) were easily separated using gravity separation. **(Figure 10c)** [53] However, calcination treatment requires expensive calcination equipment, is energy-intensive, and can emit toxic gases like HF.

Various methods can be used to pre-treat the waste lithium-ion batteries. Each method has its advantages and drawbacks, and a more scalable method needs to be matured to be used on a commercial scale.

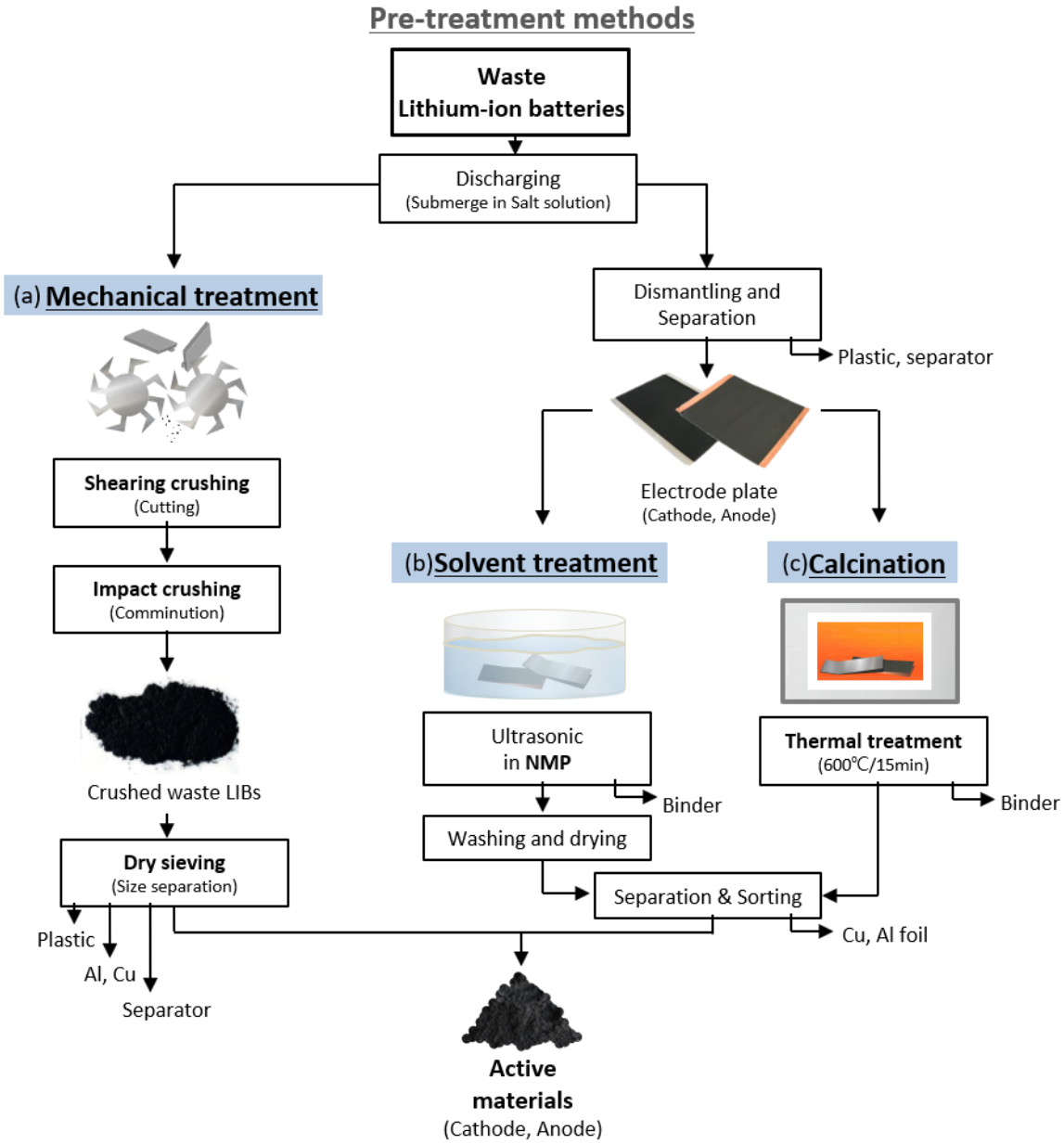


Figure 10. Pre-treatment methods for waste lithium-ion batteries

1.2.3. Current lithium recycling method: hydrometallurgy

Recently hydrometallurgy is the most common method for lithium extraction. It ionizes the lithium in the powder from pre-treated active materials with acid and bases, followed by leaching to obtain Li^+ solutions to extract lithium. Inorganic acids such as sulfuric acid, hydrochloric acid, and nitric acid are used. Heat or redox reactions using H_2SO_3, NH_2OH, H_2O_2 are applied to increase leaching efficiency. Among the redox agents, H_2O_2 is the most used reductant due to its low cost, and non-toxicity. H_2O_2 can increase the leaching reaction rate using its strong reducibility. However, using an acid with a low pH can cause the emission of harmful gases like Cl_2 and NO_x, which causes an environmental cost. Thus, research is ongoing to use weak acids such as oxalic acid or citric acid. Lithium compounds can be created using acids or bases to leach, followed by precipitation, solvent extraction, or selective adsorption. **(Figure 11)**

Precipitation

Precipitation is the most common method to separate lithium from a leached solution. This method uses the solubility difference of metal compounds which depends on specific pH and temperature. [54-74] Mainly, materials with low solubilities, such as transition metal hydroxide or oxalates, are precipitated. Therefore, precipitants such as NaOH, Na_3PO_4, Na_2CO_3 are mainly used to precipitate other dissolved metals, followed by lithium extraction in the form of Li_2CO_3 or Li_3PO_4 by reacting Li^+ and precipitants. For example, Li_2CO_3 has a higher tendency to form low-soluble Li_2CO_3 in higher pH conditions, due to the formation of CO_3^{2-} ions in high pH conditions. Also, the solubility decreases in higher temperatures (12.9g/L at 25’C, 10.8g/L at 40°C), which makes it easier for precipitation. Li_2CO_3, compared to other compounds (LiOH-129g/L, LiCl-815g/L at 25°C) has a substantially lower solubility, which makes it easier to precipitate. This method is the safest, most economical, and efficient (in retrieval efficiency) among the hydrometallurgy methods. Gao et al. precipitated Li_2CO_3 from the separated $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ electrode material. $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ was leached using 70°C 2M formic acid and H_2O_2 reductant, followed by an increase in pH using NaOH and NH_4OH solution. [61] The increase in pH precipitates Co, Mn, and Ni as hydroxides, which are separated. A saturated Na_2CO_3 solution is added to the remaining solution to create Li_2CO_3. This method, reportedly, retrieved 98.22% of the lithium. Yongxia Yang et al. used precipitation to separate lithium from $LiFePO_4$, a lithium-ion battery cathode. [62] $LiFePO_4$ cathode is difficult to leach, thus the crystal structure needs to be destroyed via calcination or chemical treatment before leaching. To destroy the crystal structure, the $LiFePO_4$ underwent ball-milling with DEDTA-2Na, and the leaching rate was increased through mechanochemical activation. Leaching was processed for 20 minutes using 0.6M of H_3PO_4 (50g/L),

followed by stirring for 9 hours in 90℃ to separate $FePO_4$, followed by adding 5M of NaOH to precipitate lithium as Li_3PO_4. Natarajan et al. obtained Li_2CO_3 from the cathode containing Co and Mn. [63] Using 3M acetic acid and H_2O_2, the anode material was leached, followed by adding $(NH_4)_2S$ to precipitate out Co as CoS, followed by adding Na_2CO_3 to precipitate Mn as $MnCO_3$. After the removal of Co and Mn, Na_2CO_3 was added to the remaining solution to precipitate Li_2CO_3.

These precipitation methods are most commonly researched, but a detailed control of operating conditions (pH, Li concentration, temperature) is needed to produce the target material.

Solvent extraction

Solvent extraction uses a two-phase system to separate lithium from the leached cathode material. It uses relative solubility to separate ions from polar and nonpolar liquids. Mainly nonpolar extractants are used to separate valuable metals (Co, Ni, Mn), and lithium is separated from the stratified solution. [75-79] Cyanex272, PC-88A, D2EHPA are used to separate Co, Ni, Mn. Zhang et al. used solvent extraction to separate lithium from $LiCoO_2$. [75] They leached the cathode material using HCl and used PC-88A to separate Co and Li ions. An increase in pH causes PC-88A to extract cobalt more efficiently. Using this trait, in pH 6.7, cobalt is separated as an organic solvent, and lithium is separated as an aqueous solution. After cobalt extraction, the separated raffinate (lithium aqueous solution) is added with Na_2CO_3 to precipitate Li_2CO_3. Chen et al. extracted lithium from $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$. [77] They leached the $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ powder using 2M H_2SO_4 in 70℃ for 90 minutes, followed by using 0.1M Na-Cyanex272 in pH 6 to separate cobalt and manganese (as organic solvent), and lithium and nickel (as an aqueous solution). Cobalt and manganese are separated from the organic solvent using 0.2M Na-D2EHPA in pH 2.95. The lithium and nickel are separated from the aqueous solution, in pH 9, using dimethylglyoxime (DMG), which has low reactivity with lithium but high reactivity with nickel in the pH 9 environment. The nickel is separated as a solid, which leaves a solution with only lithium. Na_2CO_3 is added to the solution to obtain Li_2CO_3. Recently, a compound called Cyanex936P has been developed, which can separate lithium from other alkaline metals. This has the potential to be a great extractant for lithium-ion battery recycling. Solvent extraction is a short time process than the precipitation method but requires additional extractant chemicals such as cyanex272 and PC-88A, along with expensive solvents. Also, detailed control of the condition, such as pH and solvent concentration, is needed because the extraction efficiency is greatly affected by it.

Selective adsorption

Selective adsorption separates lithium by using a lithium ion-sieve to adsorb dissolved lithium. Lithium ion-sieves are an inorganic adsorbent that is extremely selective for lithium in a lithium-containing solution and is originated from the technology to extract lithium from lithium containing solutions such as lithium brines. As lithium is the smallest metal ion, lithium ion-sieves use a vacancy to only allow lithium ions. Lithium manganese oxides (LMO) type has the highest selectivity, capacity, and stability among inorganic solvents. Also, it has low toxicity, which makes it the most common material. Wang et al. leached lithium from lithium-ion batteries using an NH_3-H_2O-NH_4HCO_3 solution with adding H_2O_2. [80] With the leached Li, Co, Ni solution, they used a manganese type lithium ion-sieve to selectively adsorb lithium. The lithium-adsorbed lithium-ion sieve was separated and the lithium is dissolved in HCl. Then NaOH and Na_2CO_3 were added to separate Li_2CO_3. This is a simple method using lithium-ion selective sieves, and allows for low contamination, but spinel-structured manganese type lithium ion-sieves are very costly and require an additional leaching process to separate the lithium combined with MnO_2.

Generally, hydrometallurgy methods guarantee high recovery rates, and do not require additional equipment, making it the most laboratory-level researched method, and closest to commercialization. However, this method requires (proportional to the lithium-ion battery) a high volume of acid and base for leaching and can cause additional chemical costs. Also, the backend costs of disposing the used solutions can be costly.

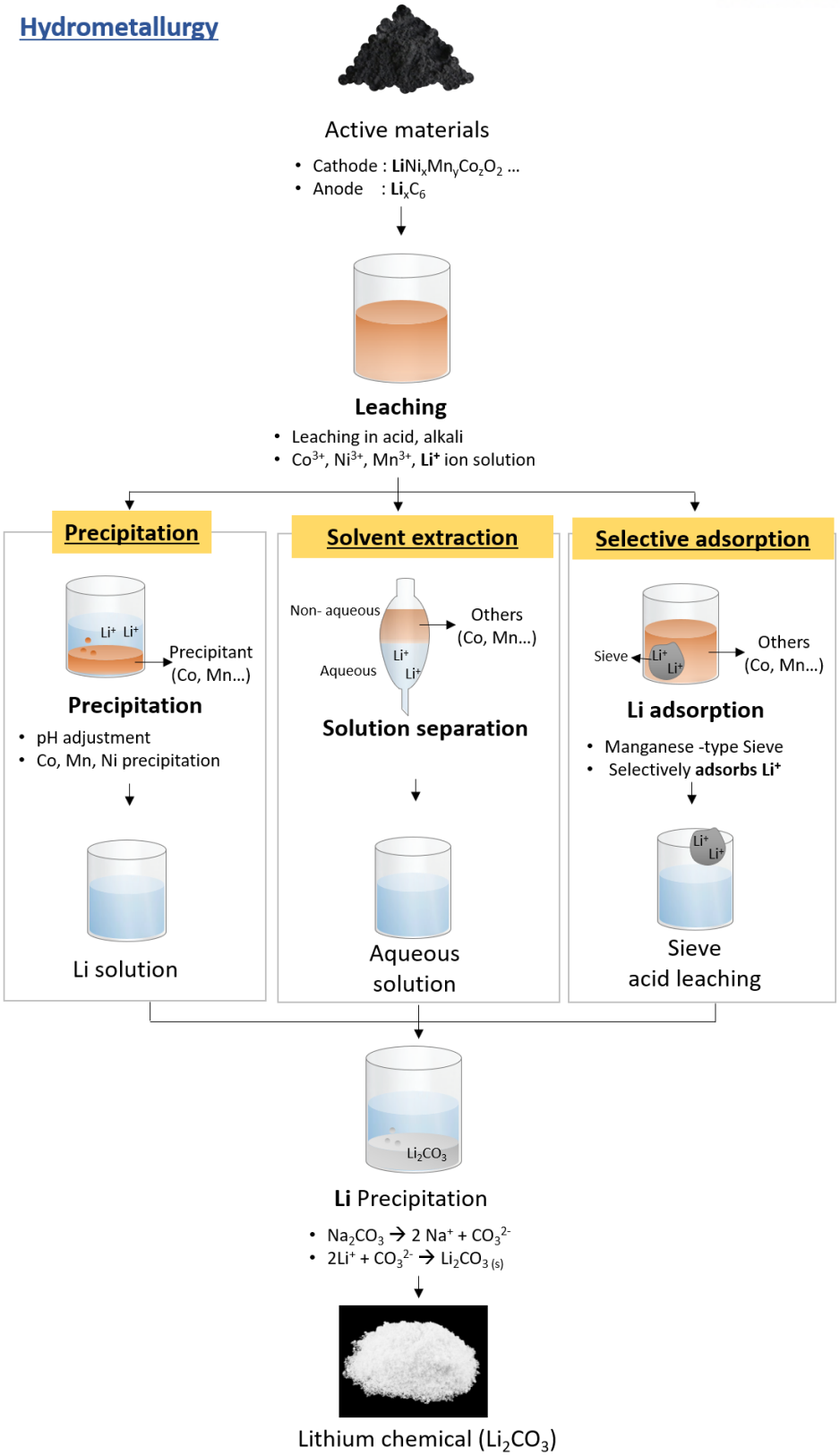


Figure 11. Current lithium recycling method: hydrometallurgy (weakness)

1.2.4. Current lithium recycling method: pyrometallurgy

Pyrometallurgy uses high temperature to remove organic material via evaporation, and cause reactions in the cathode and anode to make lithium soluble in the water. [81-90] The lithium is then recycled from the aqueous solution. The pre-treated active materials are in powder form and undergo calcination. Under a temperature normally higher than 700°C, the cathode lithium metal oxide and anode are reacted into Li_2CO_3 and metal oxides. The reactions that take place are shown in Equation 2 to 6. (Equation 2-6)

$$C + 12LiMO_2 \rightarrow 6Li_2O + 4M_3O_4 + CO_2 \quad (2)$$

$$C + 4LiMO_2 \rightarrow 2Li_2O + 4MO + CO_2 \quad (3)$$

$$2M_3O_4 + C \rightarrow 6MO + CO_2 \quad (4)$$

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \quad (5)$$

$$2MO + C \rightarrow 2M + CO_2 \quad (6)$$

The calcined powder then undergoes water leaching to dissolve lithium (in the form of Li_2CO_3) in the water. The metal oxide does not dissolve in water. After water leaching, via filtration, the undissolved metal oxide and the aqueous solution are separated to produce Li_2CO_3 solution, followed by water evaporation to finally obtain Li_2CO_3. **(Figure 12)** This method can process bulk amounts of disposed LIBs and can be simply treated via calcination. Li et al. recycled lithium via pyrometallurgy by using $LiCoO_2$ and graphite from a pre-treated LIB. [82] The separated active materials are calcined in a nitrogen condition at 1000°C for 30 minutes to obtain a Co, Li_2CO_3, and graphite compound. This compound was submerged in water to separate lithium, using wet magnetic separation. Pindar et al. separated lithium-ion batteries and calcined at 800°C for 45 minutes to create a lithium-containing powder, which was dissolved in a water mass of 50 times more than the powder mass. [87] This resulted in a Li_2CO_3 with some LiF mixed, at a 90% lithium retrieval rate. Xiao et al. used pyrometallurgy to separate lithium from $LiMn_2O_4$, $LiCoO_2$, $LiMn_xCo_yNi_zO_2$ mixed with graphite. They separated the cathode material from the battery, and calcined at 700°C in a vacuum condition for 30 minutes. The calcined powder was a metal oxide, Li_2CO_3 compound, which was then reacted with water (25g/L) for separation.

The biggest drawback of the pyrometallurgy method for lithium recycling is that additional steps are required after the calcination process. However, the low solubility of Li_2CO_3 (13g/L) requires a large amount of solvent. Also, the pyrometallurgy method requires high cost calcination equipment, and can cause the emission of harmful gases.

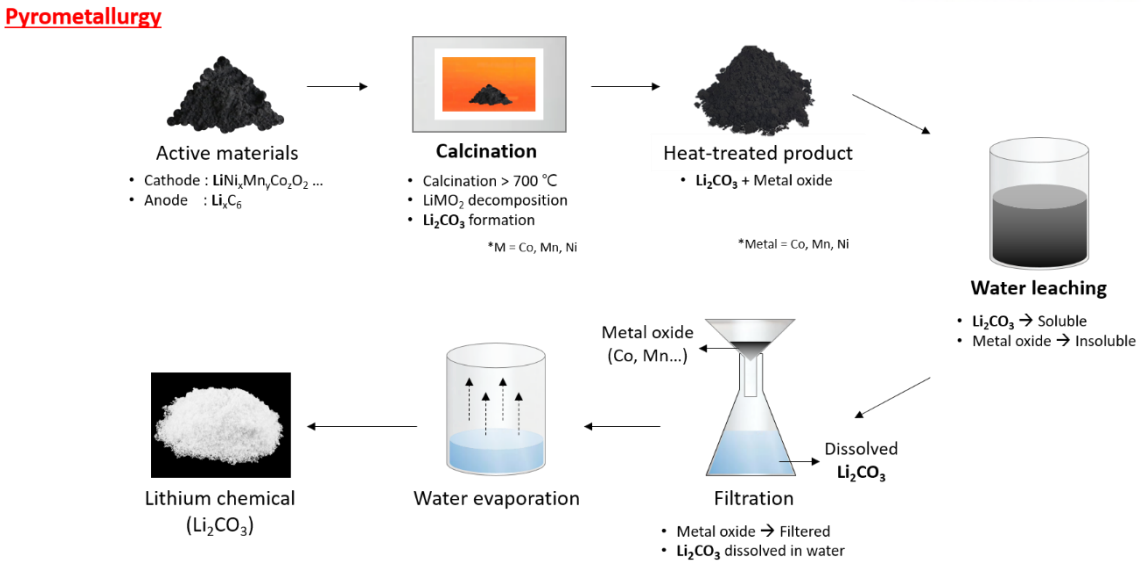


Figure 12. Current lithium recycling method: pyrometallurgy (weakness)

1.3. Issues for current lithium recycling methods

Given the circumstances, each method of lithium recycling must develop for commercialization, for a better, more sustainable lithium cycle. The following directionality is needed for a more vibrant lithium recycling market.

Currently commercialized or researched techniques can be environmentally harmful. Lithium recycling technology not only curtails lithium scarcity via recycling, but it also needs to reduce waste, to prevent environmental pollution. However, most currently developed recycling methods produce pollutants. This includes the harmful gas created by heat treating lithium waste, and acid, base, and organic solvents used for leaching. This also leads to additional costs for processing the waste. The extra cost and procedure can be a hindrance to the commercialization of lithium recycling. Thus, substantial consideration should be put into streamlining the process to minimize waste products, or to reuse the waste products from the lithium recycling processes.

The economics cannot be ignored. If purchasing cost is lower than recycling cost, recycling would not make economically proper. The current methods use acids or base, or operate in high temperature, which is usually costly and energy intensive. The more chemicals involved in the process will surely increase the cost of the process. The amount of acid and base required for lithium recycling is substantially greater than the recycled product amount, which is economically disadvantageous. Thus, methods to reuse the acid and base, or to lower the operating temperature must be developed, to minimize the cost and energy to recycle lithium. If an economically viable method emerges, this will accelerate the interest and development in lithium recycling technologies.

1.4. Previous research

1.4.1. Lithium-liquid battery

In the previous study, a lithium-liquid battery was developed using waste lithium-ion batteries. **(Figure 13)** This system consists of anode and cathode as usual battery system and these two compartments are separated with a solid electrolyte. [91] This solid electrolyte only penetrates lithium ions and blocks the other ions from penetrating. When the waste Li-ion battery materials such as cathode, anode, liquid electrolyte, was put into the cathode compartment of the LIB system, charging of the system can be operated. When charging the lithium ion from the cathode, anode, liquid electrolyte from waste LIBs goes through the solid electrolyte and form lithium metal in the anode compartment with the reaction with electrons. And with this lithium ions extracted from the waste-lithium-ion batteries charge and discharge of the lithium-liquid battery can be operated. This research proved that this battery system using waste-lithium-ion battery materials as cathode materials can operate over 20 cycles. [91] With this previous research, the idea of lithium recycling from the waste-lithium-ion battery has come out. This system can only use water as the additional chemical when extracting lithium, which has no additional chemical cost, which led it to be an economic and eco-friendly lithium recycling system.

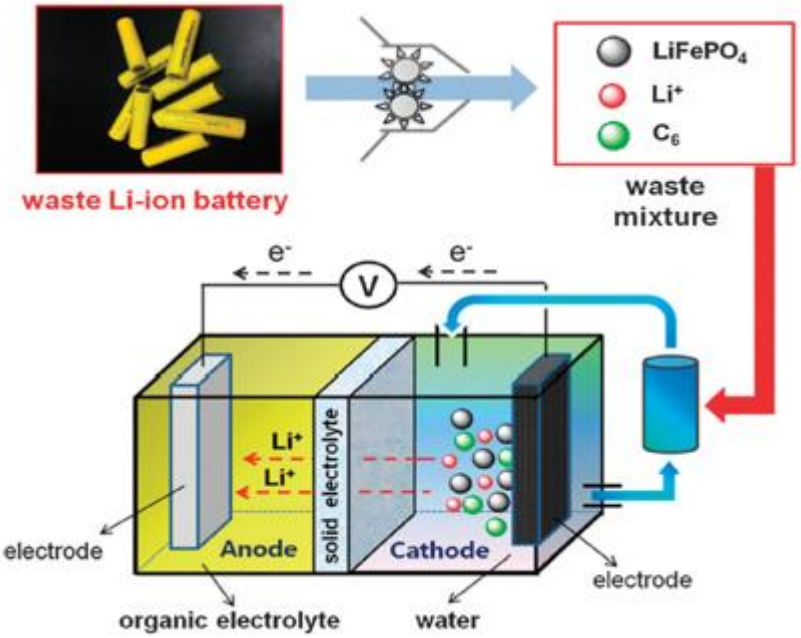


Figure 13. Lithium-liquid battery

2. Results and Discussion

2.1. Waste-To-Lithium system

An electrochemical lithium extraction system was developed, and it is named Waste-To-Lithium (WTL) system. WTL system is composed of three compartments: waste cathode, harvesting anode, and recycling cathode, and each compartment is physically separated by a solid electrolyte. **(Figure 14)** This system extracts lithium from pre-treated waste-LIB materials. Pre-treated waste-lithium-ion battery materials are first put into the water in the waste cathode and the charge of the system operates. When charging the WTL system, the waste-lithium-ion battery materials are extracted and pass through the solid electrolyte to form lithium metal or lithium ion in the harvesting anode. After charging, by discharging the separated lithium from the harvesting anode to distilled water, Li_2CO_3 can be formed via reaction with water, oxygen, and CO_2.

2.1.1. Waste lithium-ion battery material

The waste lithium-ion battery materials were collected and pre-treated at TSK pre-tech company. They collected waste lithium-ion batteries and pre-treated the batteries at 140 ºC for 15 minutes and increased them to 180 ºC. The calcined battery was separated with particle sizes, with particle size separator and the other materials such as plastic, copper and aluminum were separated. And the finest particle was separated and used as a waste powder for the WTL system. **(Figure 15a)** This waste powder was analyzed with X-ray diffraction (XRD) for material phase analysis and inductively coupled plasma (ICP) was analyzed to examine the lithium concentration and other elements contained in the waste powder.

With XRD analysis, the pre-treated black powder was examined as a mixture of $LiCoO_2$, CoO_2 and graphite. These all three components came from the waste lithium-ion battery and it can be examined that both $LiCoO_2$ and delithiated $LiCoO_2$ co-exist in the pre-treated powder. **(Figure 15b)** The diverse elements of the black pre-treated powder were also confirmed with ICP and possible elements such as lithium, cobalt, aluminum, copper, manganese, nickel were examined. The highest concentrated powder was cobalt, which came from $LiCoO_2$, and lithium was the second-highest concentrated element among other elements. **(Table 3)** Also, other elements were also analyzed, such as aluminum and copper. This indicates that a small amount of aluminum and copper is not separated from the particle size separator and mixed with active materials. However, the most concentrated elements indicate that most of the active materials are from $LiCoO_2$ active material.

Electrochemical extraction

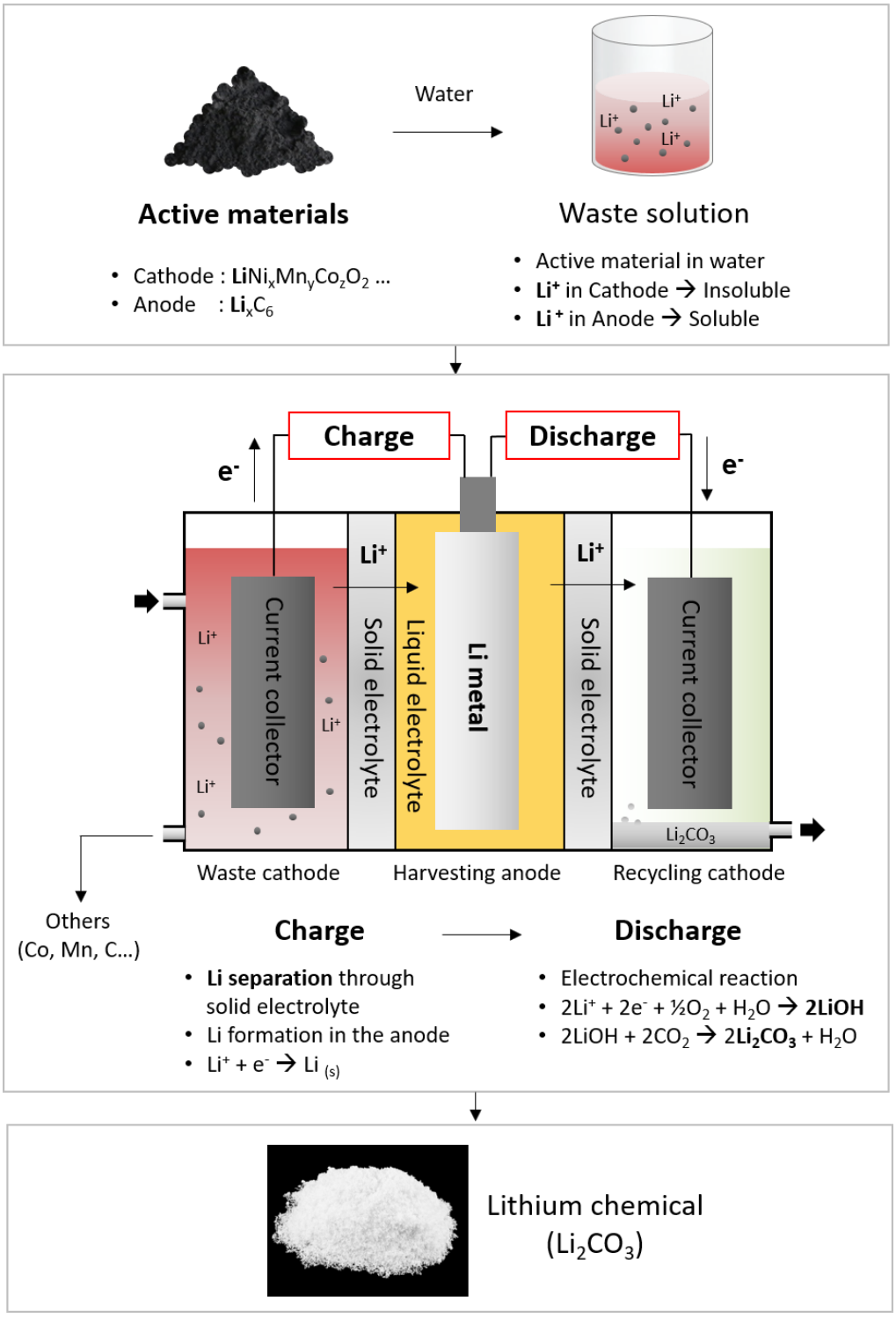


Figure 14. Waste-To-Lithium (WTL) system

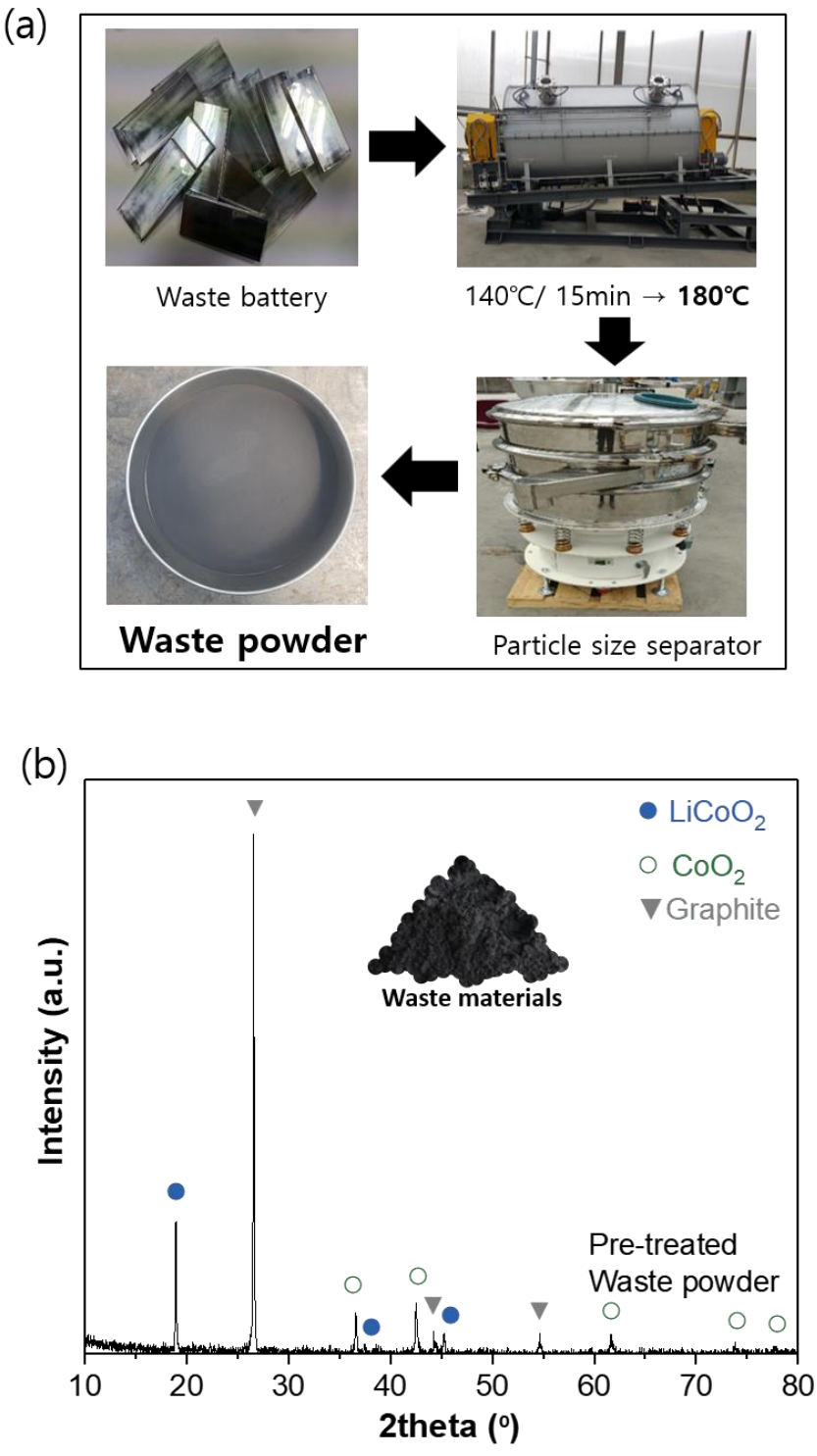


Figure 15. Waste material for WTL system

Table 3. ICP data of waste materials pre-treated from waste lithium-ion batteries.

Element	Concentration (ppm) – ICP data
Li	**33556**
Co	383288
Al	18994
Cu	415
Mn	62.5
Ni	200

2.1.2. Waste solution

The pre-treated active material powder was then put into the deionized water (D.I water) to apply in the waste cathode compartment of the WTL system. The pH of the D.I water was 7 before the pre-treated waste powder was put in. After putting pre-treated powder, the pH of the water turned into pH 12.28. Also, powder separation was occurred, which indicated that the low-density anode, graphite material, and high-density cathode, $LiCoO_2$, of a waste lithium-ion battery are mixed in the pre-treated waste powder.

And to examine the reaction that occurred after putting into the water, the powder and the solution were separated with filtration and examined independently. The powder was examined with XRD analysis it shows almost no difference with the initial pre-treated waste powder. This indicates that the cathode material has no reaction with water and doesn't deserve into the water.

The separated solution was also examined with XRD analysis after drying. When the D.I water is dried, there should be no powder left, however, the white powder was left after drying for one day. This dried powder was collected and examined with XRD. XRD shows that the dried powder was Li_2CO_3 powder, compared with JCPDS data of Li_2CO_3. **(Figure 16)** This Li_2CO_3 might originate from the LiOH, which is highly reactive with CO_2 and form Li_2CO_3. The LiOH in the water can be formed with the reaction in the Li^+ ion and water. The Li^+ ion might come from the lithiated graphite or dried lithium organic electrolyte salt in the pre-treated powder and form LiOH in the solution. Formed LiOH increases pH of the D.I water and make the solution lithium conductive.

Therefore, when the pre-treated waste powder reacts with D.I water to form a waste solution, lithium conductive solution is formed and both dissolved lithium and powder form lithium need to be extracted with WTL system.

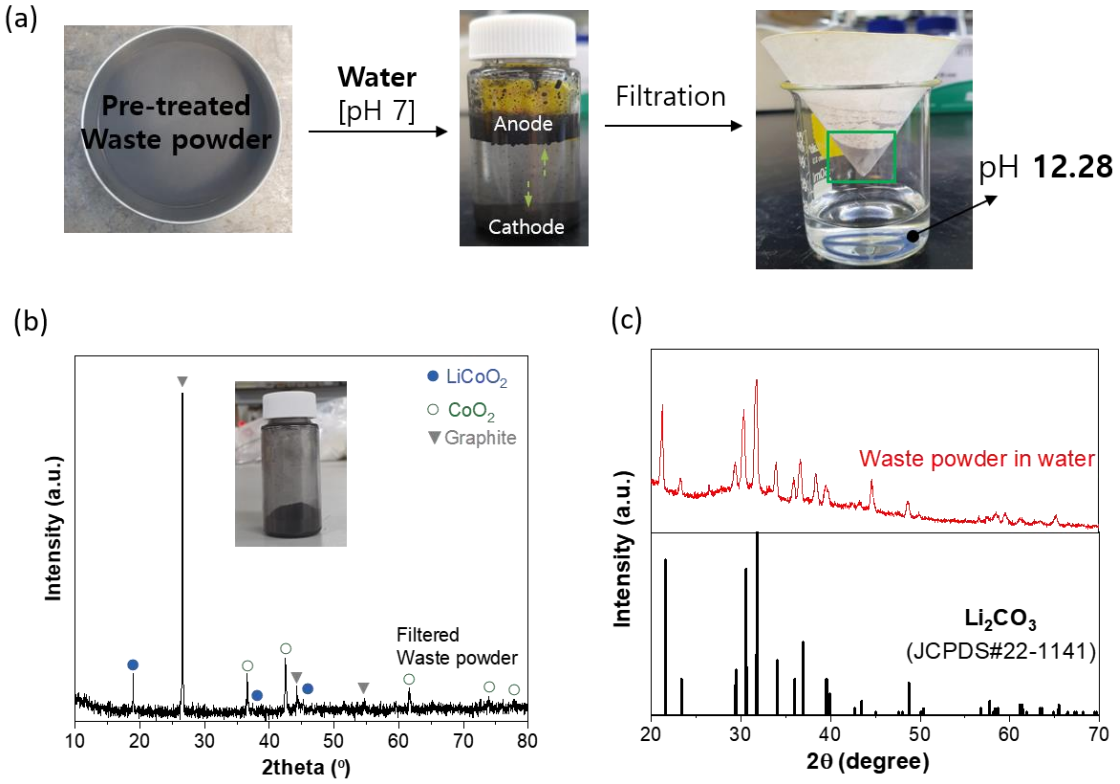


Figure 16. Waste solution properties for WTL system

2.1.3. Waste-To-Lithium cell components

As was mentioned above, the WTL system is composed of a waste cathode, harvesting anode, and recycling cathode. This WTL has three main components: solid electrolyte, current collector, anode electrode. These three components should be optimized to extract lithium from waste solution with a WTL system.

The first component, solid electrolyte conducts lithium through each compartment of the system. It should physically separate each compartment. Due to this requirement, solid electrolytes should be dense enough to block water and other ions except for lithium ion and should have high stability toward the water. Also, except the water stability, the important property needed for the solid electrolyte is ionic conductivity. Normally solid electrolyte has ionic conductivity between 10^{-3} to 10^{-6} S/cm. WTL system needs higher ionic conductivity over 10^{-4} S/cm. **(Figure 17)** Among all the lithium conductive solid electrolytes, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) contains both properties of high water-stability and high ionic conductivity. LATP has proved to be no reaction with water, and the highest ionic conductivity is 10^{-3} S/cm. However, LATP has a critical disadvantage of low sinterability. To produce the dense solid electrolyte pellet, LATP needs sintering. Due to the low sinterability, it is difficult to produce LATP pellet which makes it difficult to apply for the WTL system. Japan company, OHARA Co., (Japan) has invented lithium ion conducting glass ceramic (LICGC) which is based on LATP solid electrolyte and added Ge, Si to higher the sinterability. They used oxide precursors and used the melting quenching method to produce high dense lithium conducting solid electrolyte pellet. The ionic conductivity of LICGC is 10^{-4} S/cm and it is proven to be water stable. Thus, we applied OHARA LICGC as a solid electrolyte in the WTL system for lithium extraction from waste solution.

Table 4. Candidates for lithium ion conducting ceramic

Type	Typical composition	RT ionic Conductivity (S/cm)	Water stability
LLTO	$Li_{3x}La_{2/3-x}TiO_3$	10^{-3}	Instable
LiPON	$Li_{2.88}PO_{3.73}N_{0.14}$	$3.3x\ 10^{-6}$	Stable
	$Li_3PO_{3.3}N_{0.5}$	$2x\ 10^{-6}$	
Thio-LISICON	$Li_{10}GeP_2S_{12}$	$1.2x\ 10^{-2}$	Instable
	$Li_{10}SnP_2S_{12}$	$4x\ 10^{-3}$	
Garnet	$Li_6La_2BaTa_2O_{12}$	$4x\ 10^{-5}$	Instable
	$Li_7La_3Zr_2O_{12}$	$4x\ 10^{-4}$	
NASICON	**$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$**	**10^{-4}**	**Stable**

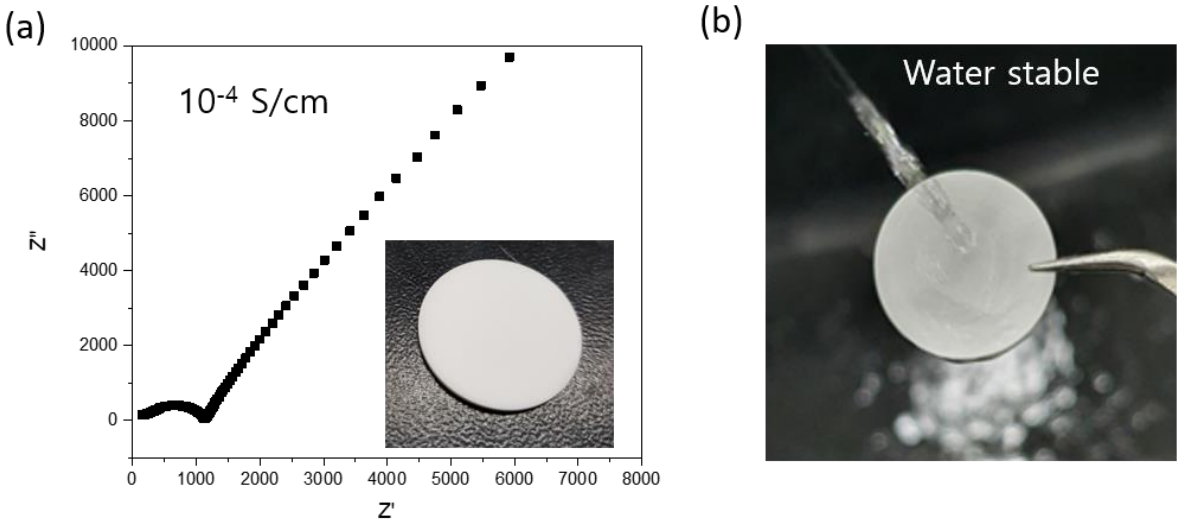


Figure 17. Cell component: Solid electrolyte

The second component is a current collector. On both waste cathode and recycling cathode, the current collector is essential for the electron pathway. The current collector on the cathode site provides reaction sites for the reaction. A current collector should possess high electric conductivity, a large surface area and needs stability toward the waste solution, and water. Among the commercialized current collectors, fibered carbon materials were applied. These carbon materials have good electric conductivity and have a large surface area. The price of carbon materials is low, which makes it easier for the application.

As the WTL system operates in the aqueous solution, a current collector needs to be hydrophilic for the stable reaction of a current collector. However, the surface of carbon materials is not hydrophilic because of the polymer agents contained to make the mechanically stable form. Thus, calcination of the carbon current collector can form C-O or C=O bonds on the surface of the carbon materials and make them hydrophilic. **(Figure 18)** Carbon felt purchased from Dissol corporation (Korea) was selected as carbon current collector as it had high electric conductivity and large surface area. It was calcined at 500°C for 4 hours in ambient air and slowly cooled down. After the heat-treatment, carbon felt showed hydrophilic characteristics examined by dropping a drop of water. This second key component of the heat-treated carbon current collector was applied to the WTL system as a current collector on both waste cathode and recycling cathode.

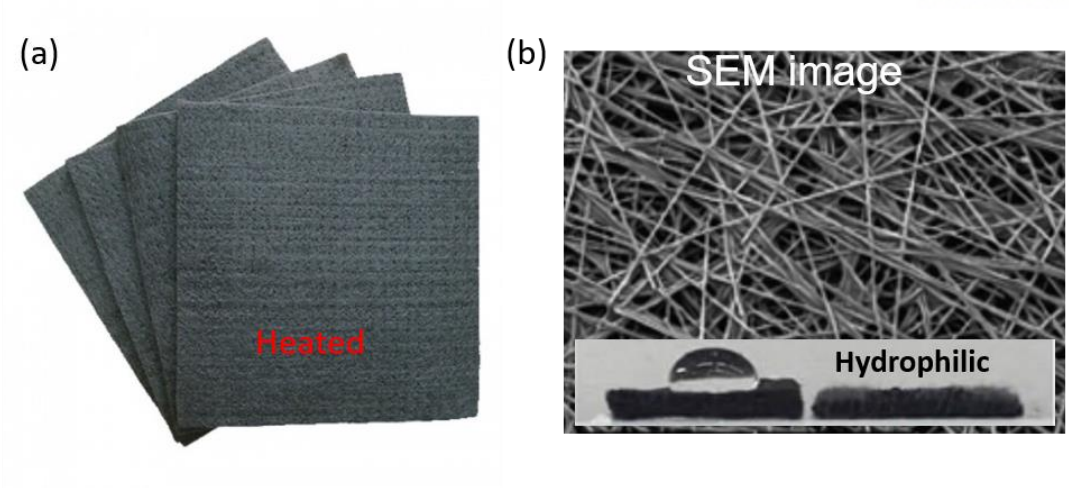


Figure 18. Cell component: Current collector

The third main component for the WTL system is the anode electrode. Anode materials can lithiate the extracted lithium after charging and delithiate the extracted lithium when discharging. Thus, this anode material needs a property to stably lithiate/delithiate lithium ions. Among the lithium anodes, graphite material is examined as an anode material. Graphite is a well-known material for lithium-ion battery anode material. It produces a stable solid electrolyte interphase (SEI) layer during the cycle of charging and discharging the lithium-ion battery and able the stable lithiation and delithiation.

Graphite powder was first mixed with low content of carbon black and a polymer binder. Carbon black was added to make the anode electrode more electric conductive, and polymer binder was added for the contact of the graphite, other powders and foil. This powder is then mixed in N-Methyl-2-pyrrolidone (NMP) solvent to produce a black-colored slurry. The slurry is then cast on the copper foil for electric conductivity and applied as the anode material. With the coin-type half-cell fabricated with Li metal and $LiPF_6$ ED: DMC liquid electrolyte, graphite showed a stable cycle over 100 cycles. **(Figure 19)** This fabricated anode electrode was applied to the WTL system using $LiPF_6$ ED: DMC as electrolyte at the harvesting anode.

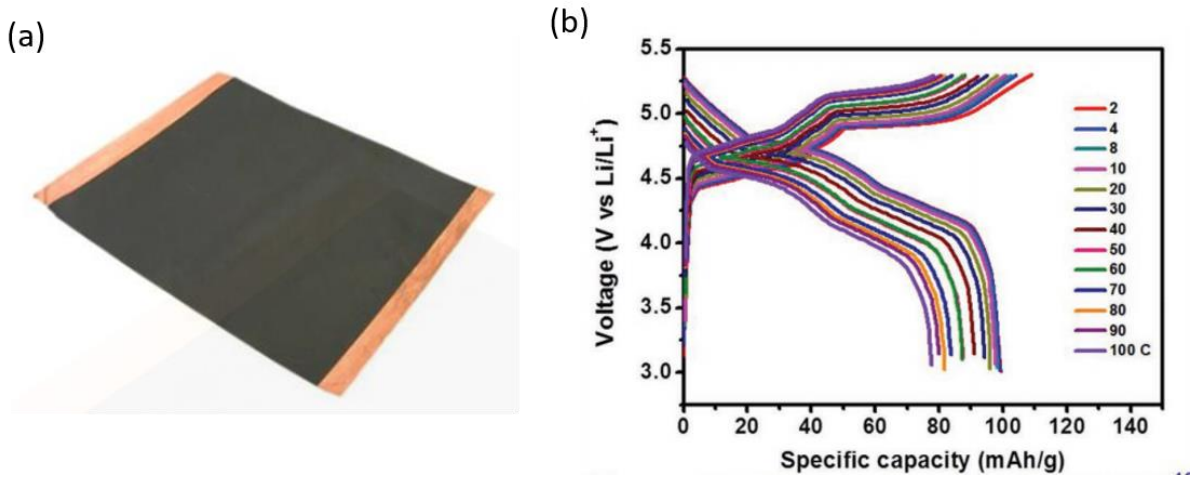


Figure 19. Cell component: Anode

2.1.4. Design of prismatic Waste-To-Lithium system

A primitive WTL cell was fabricated with the coin-type harvesting anode. The cap and bottom of the coin-type cell were fabricated with the key components, solid electrolytes, and anode to make a coin-type harvesting anode. The spring and liquid electrolyte were also contained to lower contact resistance. This harvesting anode was fabricated with a current collector and cathode cap and anode bottom to fabricate a primitive WTL cell.

For charging, the waste solution was put in the cathode compartment. And the lithium from the waste powder and solution was extracted when charging. In contrast, when discharging, distilled water was filled instead of waste solution to recycle extracted lithium after charging. **(Figure 20)**

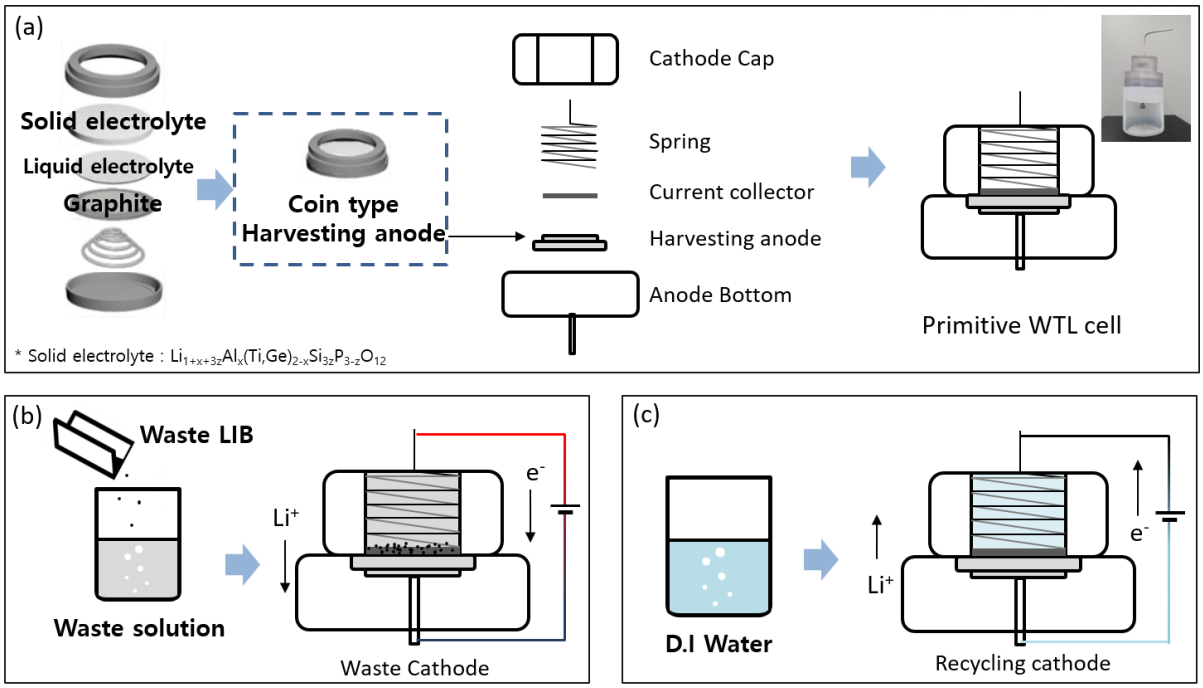


Figure 20. Prismatic WTL system for mechanism investigation

2.2. Mechanism of Waste-To-Lithium system

WTL system can extract lithium from waste lithium-ion batteries and recycle in the form of Li_2CO_3. The detailed mechanism should be examined for the further development of WTL system. To investigate the mechanism, a developed coin-type primitive WTL system was used as the reference system. Charge and discharge of the system were operated with 3 mL of the waste solution and D.I water for the fast mechanism investigation.

2.2.1. Charging mechanism of Waste-To-Lithium system

As explained above, when the pre-treated active material is put in water to make a waste solution, the lithium in the cathode powder does not dissolve, while some lithium in anodes and dried liquid electrolyte dissolves in water to form LiOH(aq). Through charging, the dissolved and undissolved lithium can be separated via the ceramic solid electrolyte, to intercalate into graphite anode. When the charge occurs, water dissolved Li^+ is expected to be separated with the oxygen evolution reaction (OER). (Equation 7) **(Figure 21)**

$$2LiOH \rightarrow 2Li^+ + 2e^- + \tfrac{1}{2}O_2 + H_2O \quad (7)$$

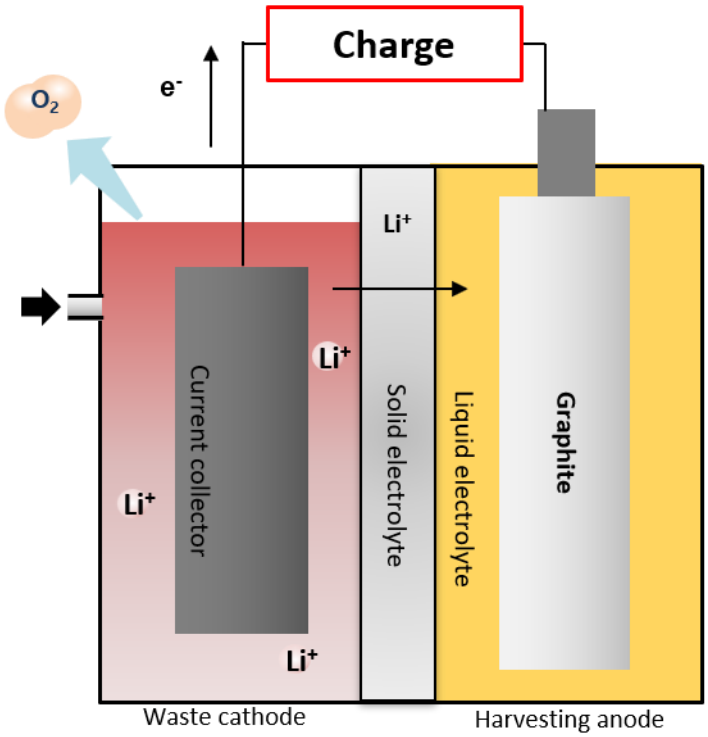
And for the undissolved Li^+ in cathode powder, it is expected to be separated by the same reaction as that of delithiation in the cathode material. (Equation 8-9) **(Figure 22)**

$$LiMO_2 \rightarrow Li^+ + e^- + MO_2 \quad (M= Co, Mn, Ni) \quad (8)$$

$$LiFePO_4 \rightarrow Li^+ + e^- + FePO_4 \quad (9)$$

The charging potential differs depending on the type of cathode material of the waste active material. When the active material is put in water, the aqueous solution becomes a strong base due to the influence of LiOH. The OER during charging differs in operating voltage depending on the pH and in strong base condition (> pH11), OER occurs below 3.6V. **(Figure 23)** [92] In the case of $LiFePO_4$ cathode powder, the delithiation reaction potential is 3.5 V, which is lower than the voltage of OER in a strong base, and Li^+ is directly extracted from the cathode powder. However, for $LiCoO_2$ (3.9 V),

$LiMn_2O_4$ (4.0 V), $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ (3.7 V), since the delithiation potential is higher than that of the strong base OER reaction, Li^+ extraction from the solution occurs first, rather than Li^+ extraction from the cathode powder. However, when charging, the pH of the aqueous solution decreases due to the characteristics of the OER reaction, and the operating voltage of the OER reaction gradually increases. And when the potential of the OER reaction becomes higher than that of the cathode powder material, Li^+ extraction from the powder becomes possible. Through this OER reaction and reaction for each cathode material, Li^+ in the form of both solution and powder can be extracted and separated, and when Li^+ cannot be extracted anymore, charging of the system is automatically finished.



$$2Li + 2OH^- \rightarrow 2Li^+ + 2e^- + \tfrac{1}{2}O_2 + H_2O$$

(OER reaction)

Figure 21. Charge mechanism from solution (equation)

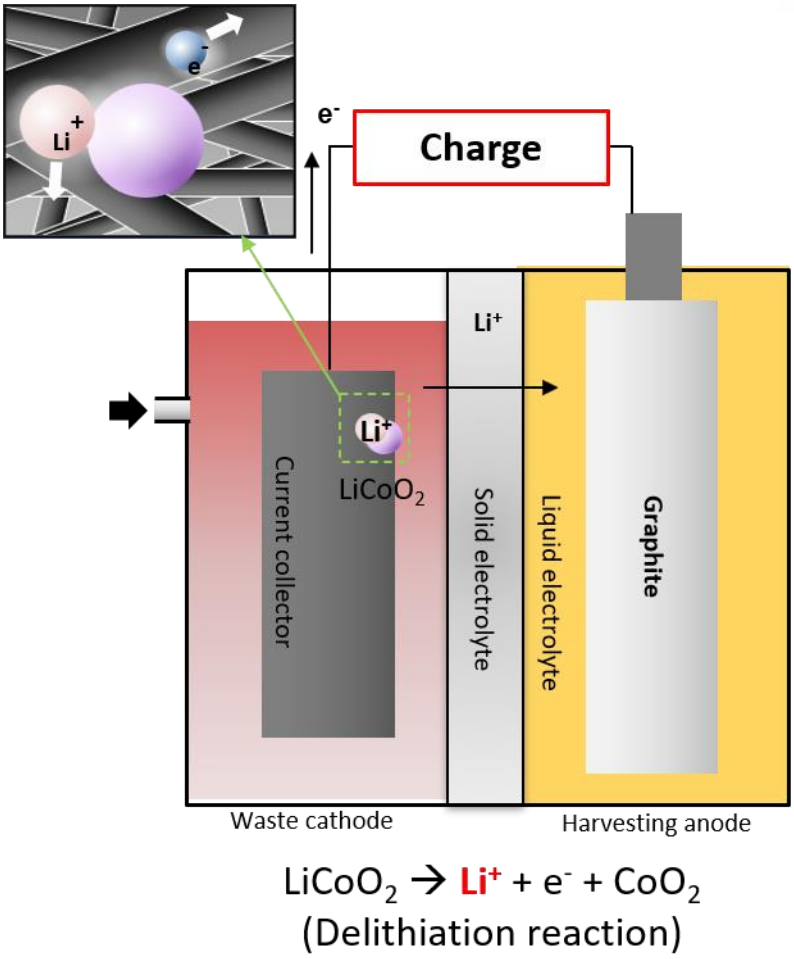


Figure 22. Charge mechanism from powder (equation)

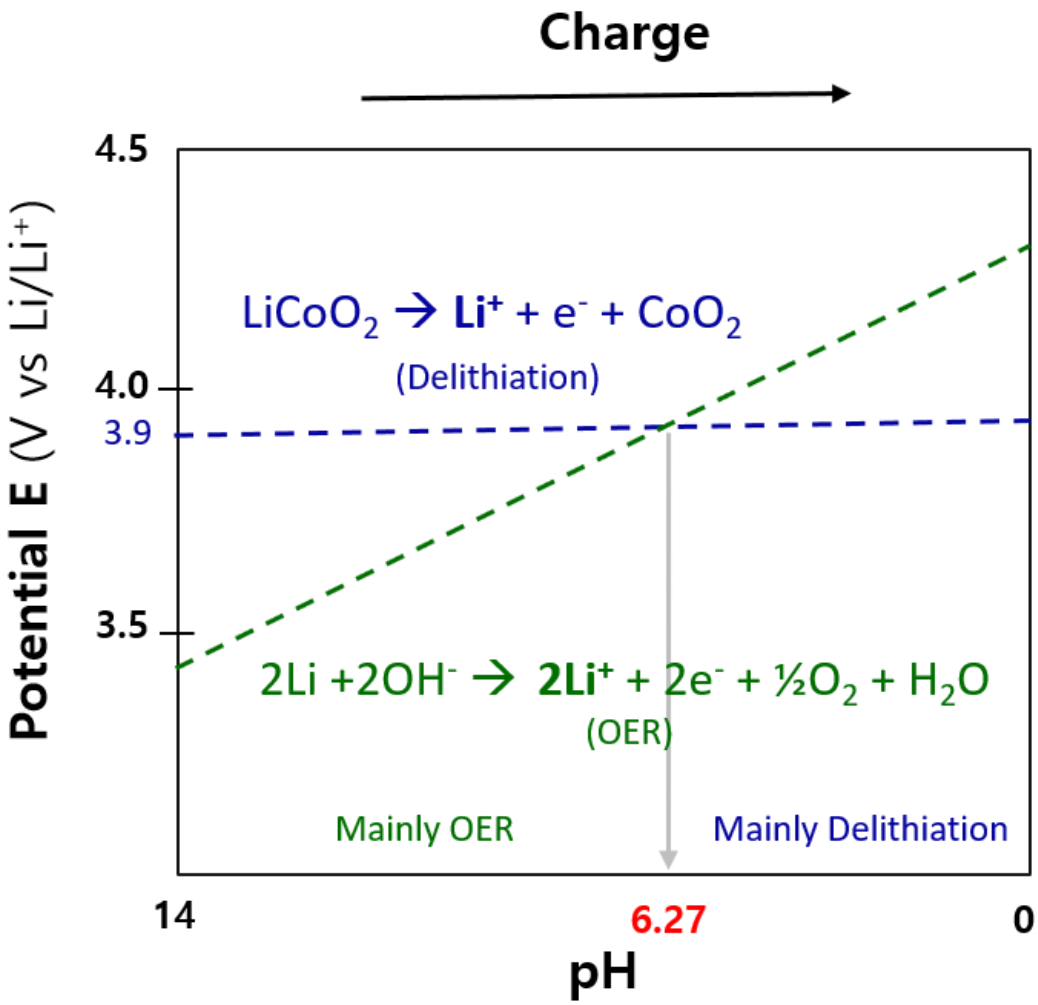


Figure 23. Theoretical potential of OER and delithiation reaction of $LiCoO_2$

To demonstrate the mechanism, a waste solution was put into the waste cathode compartment. The charging was operated with a constant current of 0.05 mA. The charge was operated for almost 600 hours and the voltage profile showed in **figure 24**. The initial pH of the solution was 12.28, and the initial potential showed near 3.5 V and slowly increased. And near 3.9 V, the slope of the increasing potential slightly decreases which can be indicated as delithiation reaction from $LiCoO_2$. After few hours of charging slope slightly increased as similar slope to the initial slope, which can be comprehended as the OER n after all the possible lithium from $LiCoO_2$ is extracted. With the experimental voltage profile, it can be roughly expected that the lithium from both powder and solution was extracted after the charging process.

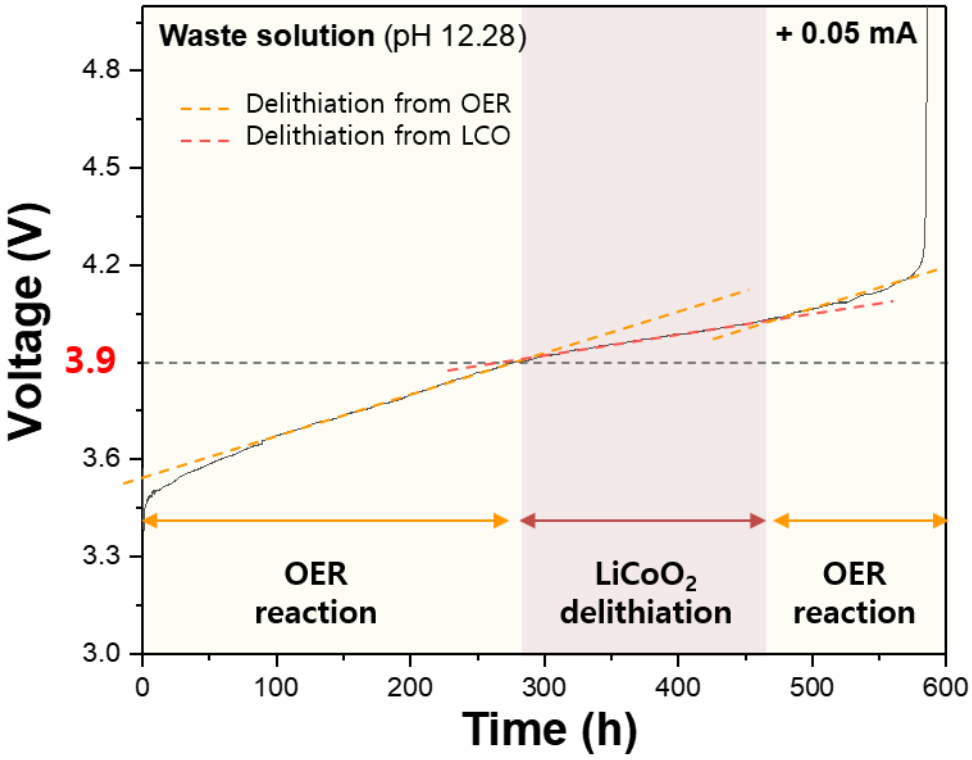


Figure 24. Charge voltage profile of WTL system (pH decrease)

For the further demonstration of the mechanism, other analyses such as ICP and XRD were used. Lithium concentration of initial waste powder was examined with ICP and lithium dissolved and undissolved from waste powder, after putting into water, was separately examined. It showed that the initial lithium amount of total waste powder was 9.26 mg and among the lithium, 5.63 mg was dissolved into water. For comparison, lithium concentration after charging was confirmed with the solution and powder separation. It showed that only 1.65 mg was left after charging, and for the solution, 96 % of the lithium was extracted. However, for the powder, only 61.4 % of the lithium was extracted. **(Table 5)** This difference might come from the kinetical resistance difference of solid-liquid and liquid-liquid and usually kinetic resistance is higher in solid-liquid, which makes it more difficult to extract the lithium from the powder than the solution. Totally 82.2 % of the lithium is calculated to be extracted from pre-treated waste powder after charging. **(Figure 26)**

In addition, XRD was also examined to compare the phase difference after charging. In XRD data, the peak of $LiCoO_2$ slightly shifted to the lower angle after charging, which indicates the delithiation of the $LiCoO_2$. This also can be evidence that the lithium from the powder was properly extracted. **(Figure 25b)**

Table 5. Lithium amount change of powder and solution after charging

Li source	Initial Li amount (mg)	Extracted Li amount (mg)	Final Li amount (mg)
		ICP data	
Dissolved solution	5.63	5.38	0.25 **[95.6 %]**
Remain powder	3.63	2.23	1.39 **[61.4 %]**
Total waste powder	9.26	7.61	1.65 **[82.2 %]**

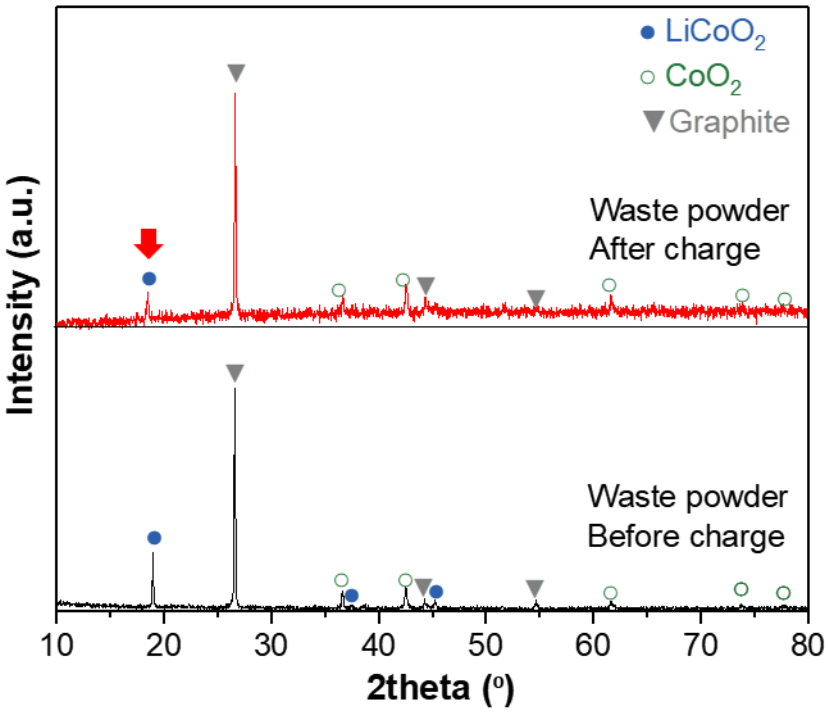


Figure 25. Change of XRD data of waste powder after charging

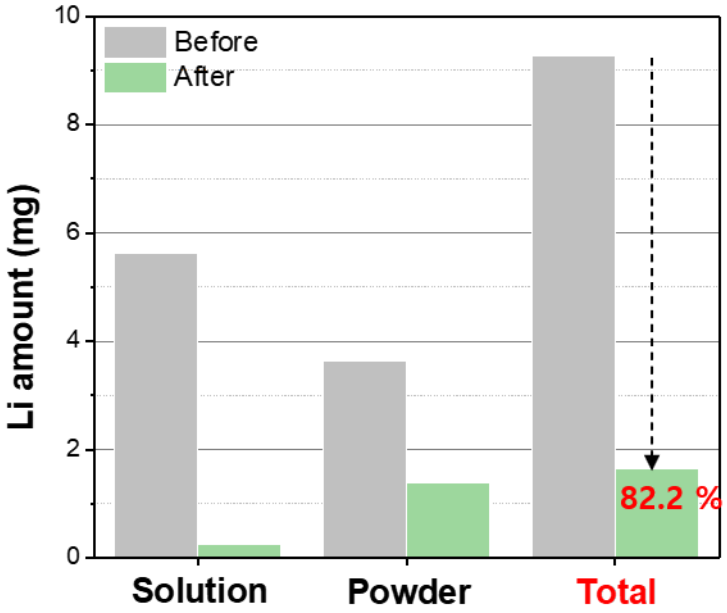


Figure 26. Lithium extraction after charging (ICP data)

2.2.2. Discharge mechanism of Waste-To-Lithium system

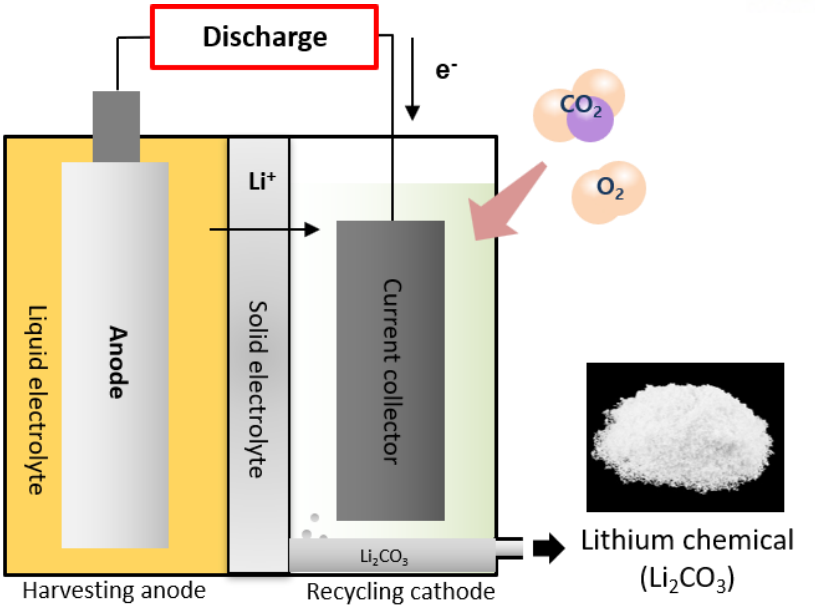
After charging, the separated Li^+ is discharged to water and passes through another ceramic solid electrolyte and expected to undergo an oxygen reduction reaction (ORR) with water and electrons to form an aqueous LiOH solution. (Equation 10,11) **(Figure 27)**

$$½O_2 + 2e^- + H_2O \rightarrow 2OH^- \quad (10)$$

$$2Li^+ + 2OH^- \rightarrow 2LiOH \quad (11)$$

To examine the discharge mechanism, discharge of the WTL system was operated after charging. For discharging only water and electron can be the candidate for the mechanism reaction, ORR is the most expected reaction. When ORR occurs, the pH of the solution increases thus the reaction potential decreases. The voltage profile shows the slow potential decrease during discharging and this indicates the ORR. Furthermore, the initial pH of the D.I water was 7.2 and after discharging, the pH has increased to 10.2. This potential decrease and pH increase can be explained as an ORR. **(Figure 28)**

To investigate the recycled lithium, the lithium amount of the discharged solution was investigated with ICP analysis. The initial lithium amount was 0 mg, as it was D.I water, after discharging, the calculated lithium amount was 7.53 mg. This indicates that with the ORR reaction, lithium was properly recycled from extracted lithium. **(Figure 29)**



$2Li^+ + 2e^- + ½O_2 + H_2O \rightarrow 2LiOH$ (ORR reaction)

$2LiOH + CO_2 \rightarrow Li_2CO_{3\,(aq)} + H_2O$

Figure 27. Discharge mechanism

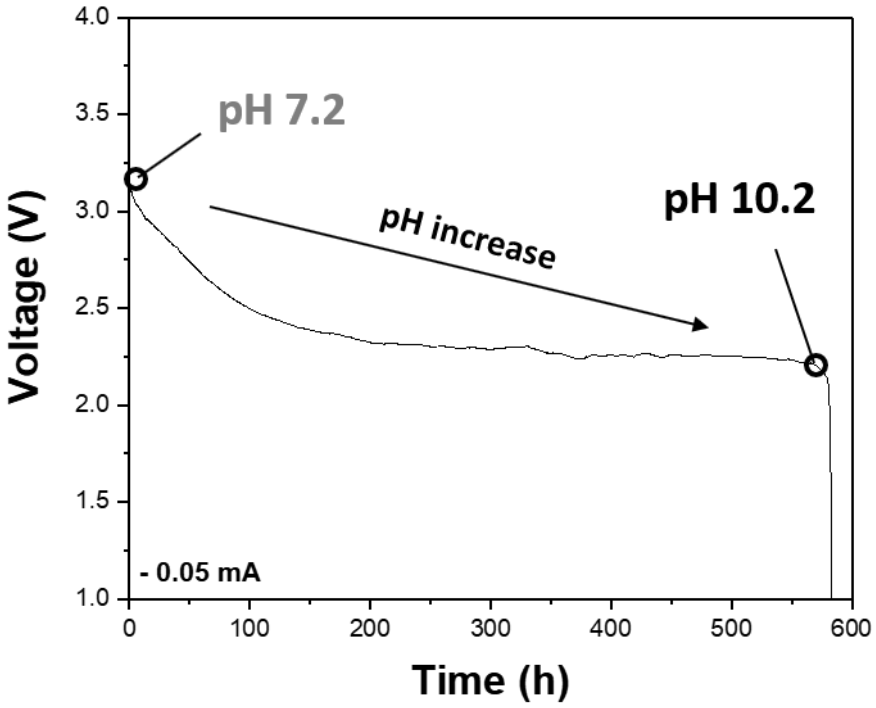


Figure 28. Discharge voltage profile of WTL system

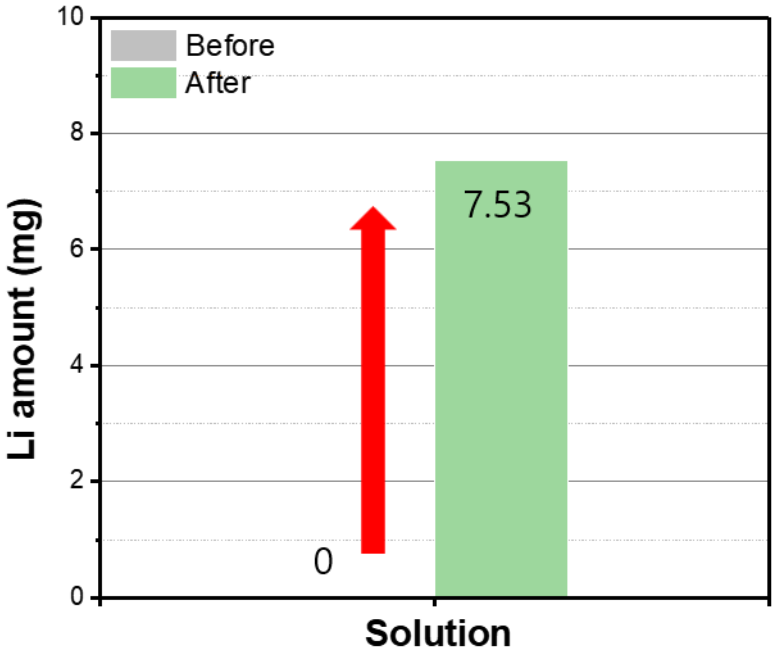


Figure 29. Lithium concentration change after discharge

After discharging to examine the recycled lithium, the discharged solution was dried at 80 ℃ for 24 h. The white crystallized powder was formed after the complete dry of the solution, and it is collected for analysis. XRD was applied to examine the powder and compared with the reference data of Li_2CO_3, it showed that Li_2CO_3 was formed after the discharging. **(Figure 30)**

As LiOH is a strong base material and is highly reactive with CO_2 enough to be used for CO_2 capturing materials, and chemically reacts with carbon dioxide to form Li_2CO_3. At the high pH (> pH 10.3) of the solution, the form of the CO_2 in the solution is CO_3^{2-} ions and it reacts with Li^+ in the solution and can form Li_2CO_3. The Li_2CO_3 forming equation is as follows (Equation 12,13)

$$2LiOH + CO_2 \rightarrow 2Li^+ + CO_3^{2-} + H_2O \quad (12)$$

$$Li^+ + CO_3^{2-} + H_2O \rightarrow Li_2CO_3 + H_2O \quad (13)$$

Thus, when discharging with the ORR reaction, LiOH(aq) is form and it chemically reacts with CO_2 to form Li_2CO_3.

To examine that the CO_2 is reacted with discharged solution, we compared the CO_2 concentration during discharging. In a completely sealed container, the solution was discharged inside to see the CO_2 concentration decrease. Atmospheric CO_2 was about 500 ppm and when 0.1M LiOH was put in CO_2 decreased sharply to 0 ppm. When discharging with 0.05 mA, CO_2 concentration showed a slow decrease and after few hours CO_2 concentration was almost 0 ppm. This graph shows that CO_2 reacts with the solution when discharging, which indicates that Li_2CO_3 has formed from the reaction of the discharged solution and the CO_2. **(Figure 31)**

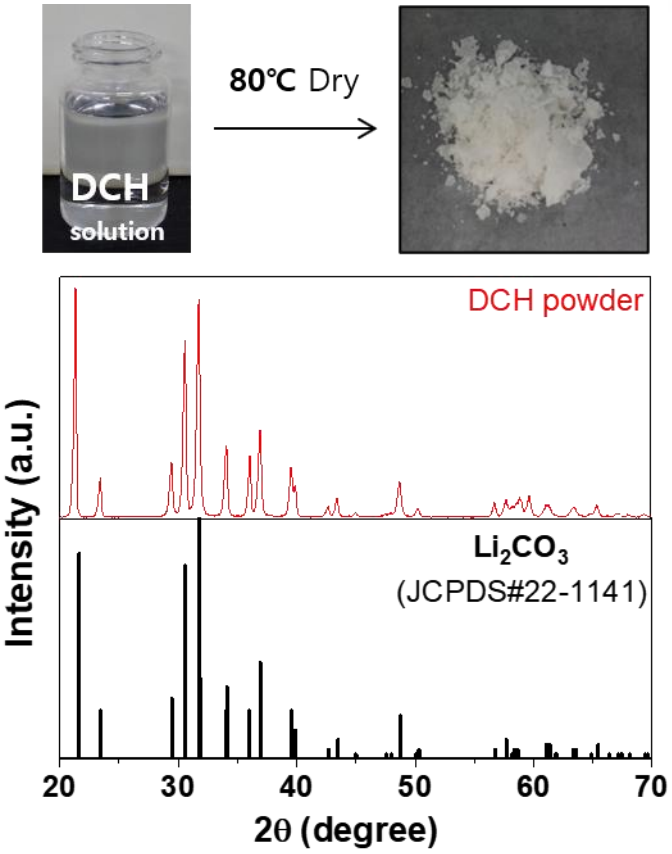


Figure 30. Lithium carbonate formation after discharging

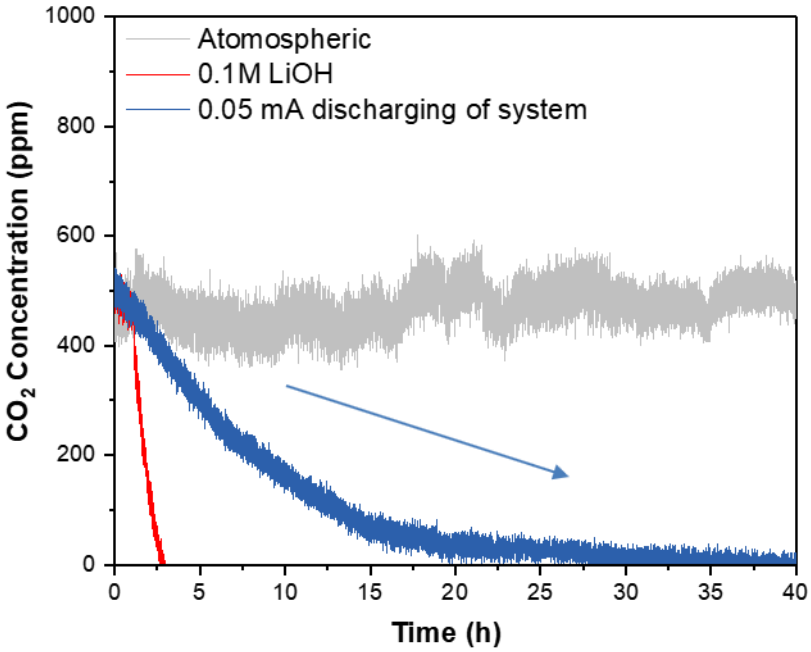


Figure 31. Carbon dioxide concentration decrease when discharging

2.3. Efficiencies of Waste-To-Lithium system

Lithium recycling efficiency and energy efficiency are calculated based on the analysis data.

For the lithium recycling efficiency, the initial lithium amount of waste powder was calculated from the ICP data and compared with the lithium amount calculated from the ICP data of the solution after discharging. The initial waste lithium amount was 9.26 mg and after charging only 1.65 mg of the lithium was left in the waste material. And after recycling the lithium with discharging the WTL system, 7.53 mg of the lithium was recycled. By comparing the initial and final lithium amount, it can be calculated that 81.3 % of the total lithium is extracted from the WTL system operation. **(Figure 32)**

To calculate the energy efficiency, the energy consumption of electric energy during charging and discharging and heat treatment was separately calculated. For the electric energy efficiency, the energy spent for charging and energy produced from discharging was calculated. It was calculated that 4×10^{-5} kWh was spent during 7.53 mg of lithium recycling. Therefore, extracting 1 g of the lithium might spend 5.3×10^{-3} kWh. **(Figure 33)**

In addition, WTL needs water evaporation to obtain the final product of Li_2CO_3. Thus, the WTL system needs additional energy consumption for heat-treatment process. For the water evaporation after discharging, it needs 0.06 kWh. Compared to electric energy needed to recycle lithium, it requires, more than 1,000 times more energy to obtain Li_2CO_3.

Totally, the WTL system needs 0.06 kWh of energy to recycle 81.3 % of the lithium from waste lithium powders.

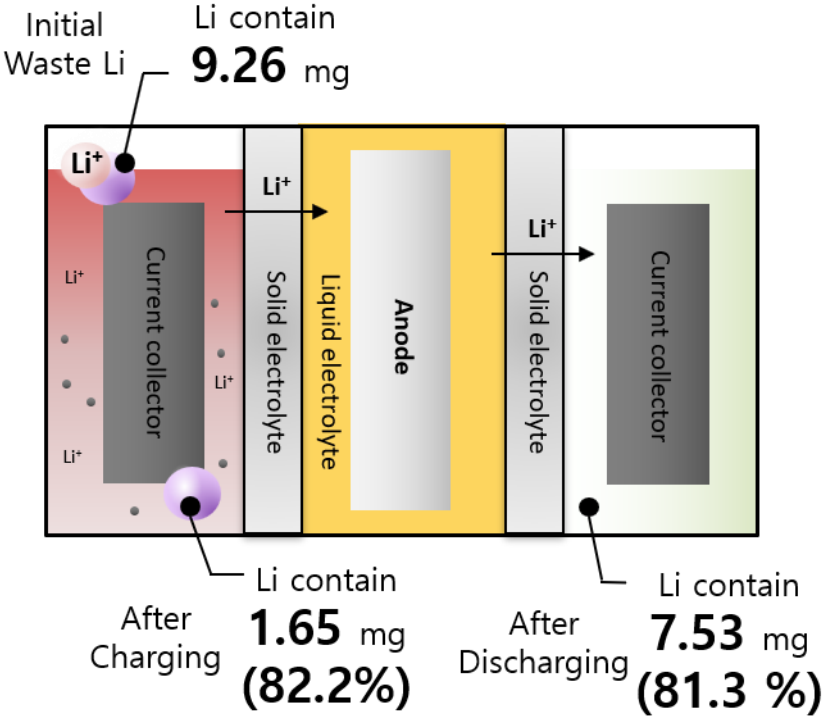


Figure 32. Total lithium extraction efficiency after WTL system

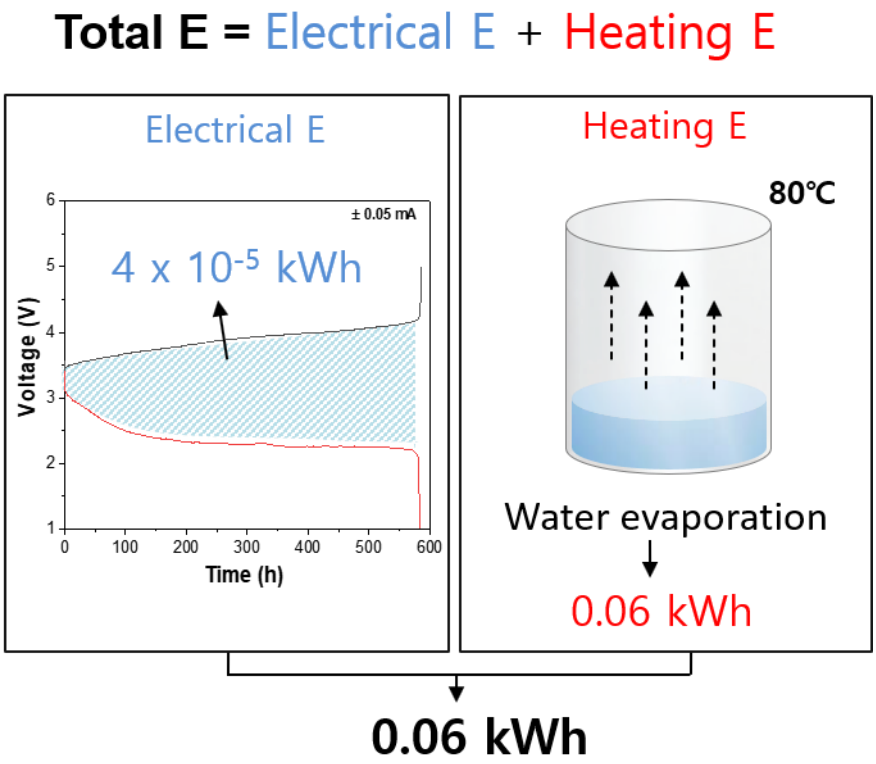


Figure 33. Energy efficiency for WTL system (High drying energy)

2.4. Saturation of lithium carbonate during discharging

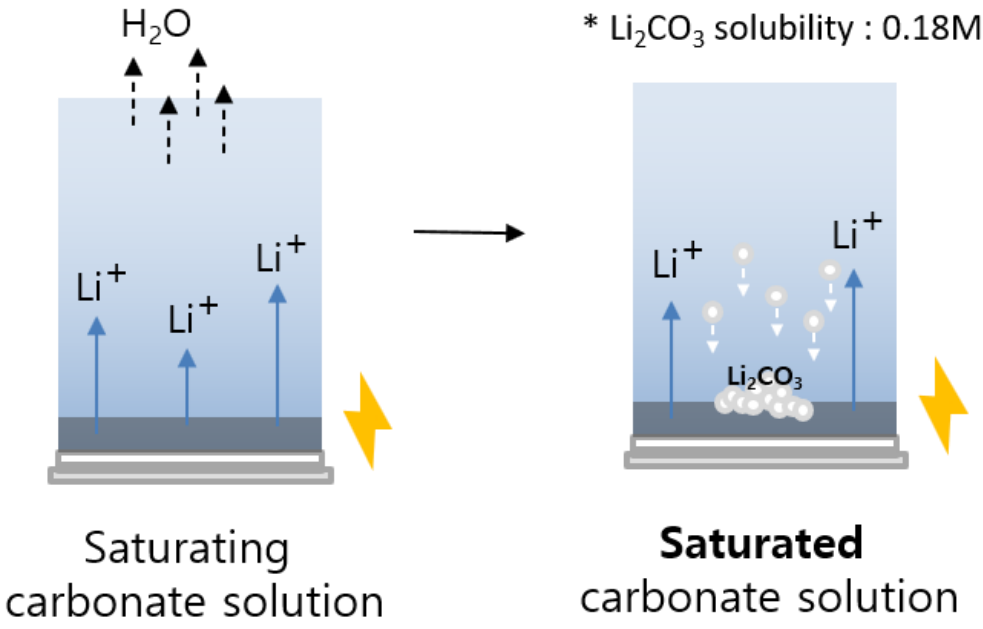
As explained above, heat-treatment energy takes 99.9 % of the total energy consumption for operating the WTL system. Due to this reason, to lower the energy consumption and to make the process simpler, the heat-treatment process to make dries Li_2CO_3 powder, needs to be excluded.

WTL system can obtain Li_2CO_3 powder without using drying or precipitation. When the system is continuously discharged Li_2CO_3 can naturally precipitate. When discharging occurs, the concentration of Li^+ in the water gradually increases, followed by the concentration increase of Li_2CO_3. In addition, due to the ORR reaction consumption of H_2O occurs and the concentration of Li_2CO_3 increases relative to the solvent decrease. Li_2CO_3 has low water solubility (0.18 M) and can easily saturated chemical. This leads to the natural precipitation of Li_2CO_3. Therefore, theoretically, by continuously discharging, heat-treatment for drying Li_2CO_3 can be excluded, and naturally, Li_2CO_3 can be saturated as powder form. **(Figure 34)**

For the demonstration, the discharge process with 0.05 mA was continuously operated in the transparent container. As shown in figure 35, the picture of the container was taken every 100 h. As the discharge operates, the solution showed a constant decrease. And near the surface of the solution, white powder formation was shown slowly. And after 600 h of discharging all the solution was reacted as ORR reaction and only white powder on the surface of the container was left. **(Figure 35)**

This white powder was collected and with an XRD analysis, it was confirmed to be Li_2CO_3 material.

By using constant discharging with ORR and low Li_2CO_3 solubility, 99.9% of the energy can be conserved for operating the WTL system. **(Figure 36)**



$$Li^+ + 2e^- + ½\ O_2 + H_2O\downarrow \rightarrow 2LiOH_{(aq)}\uparrow$$

- Water elimination (ORR)
- Li^+ concentration Increase

Figure 34. Methods for lowering energy efficiency

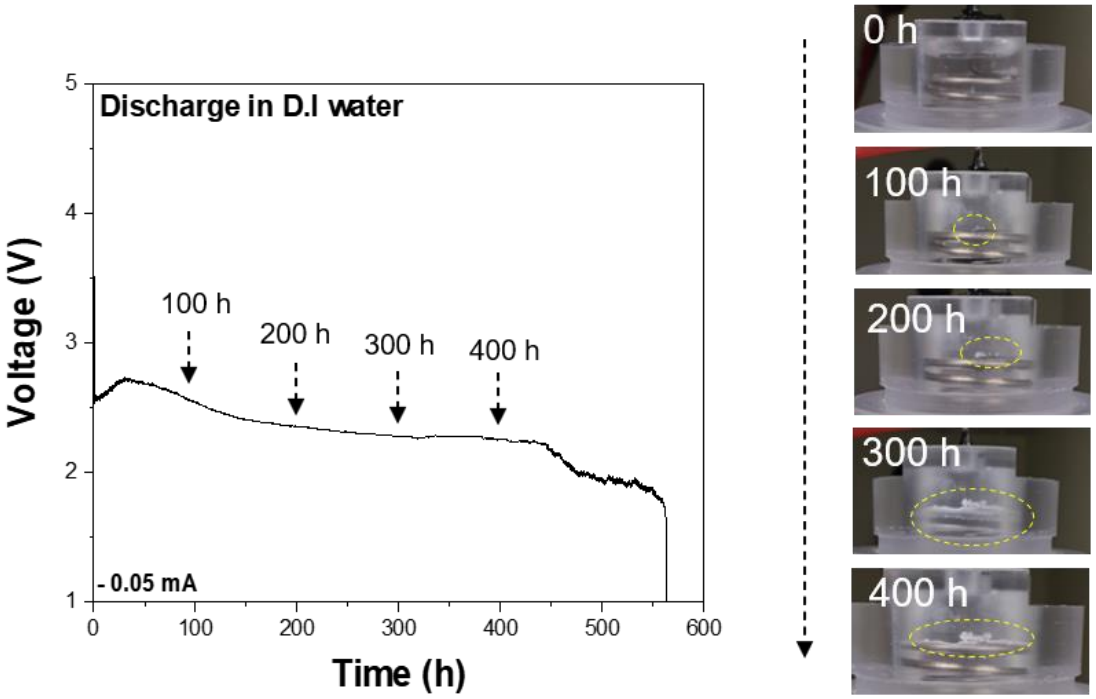


Figure 35. Lithium carbonate formation with saturation (XRD)

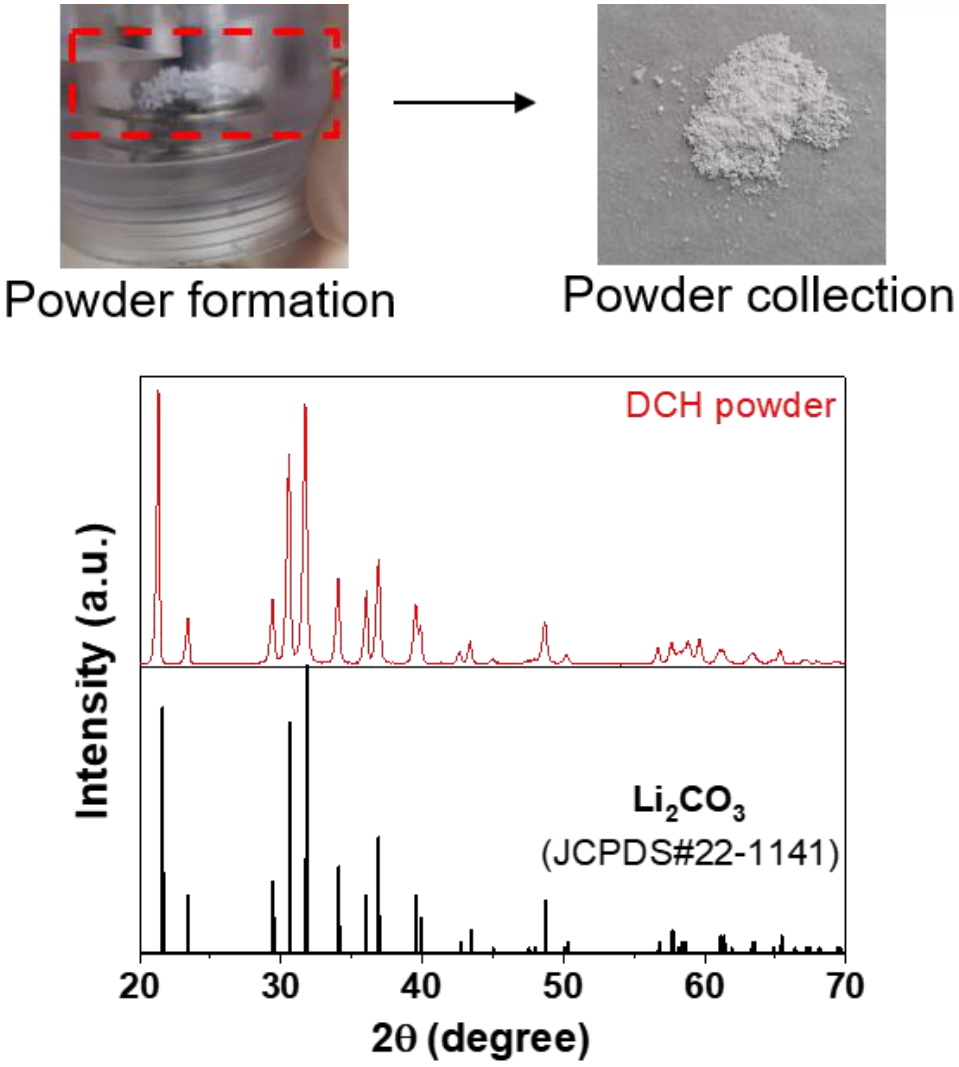


Figure 36. XRD analysis for saturated lithium carbonate

2.5. Development of square-type WTL system

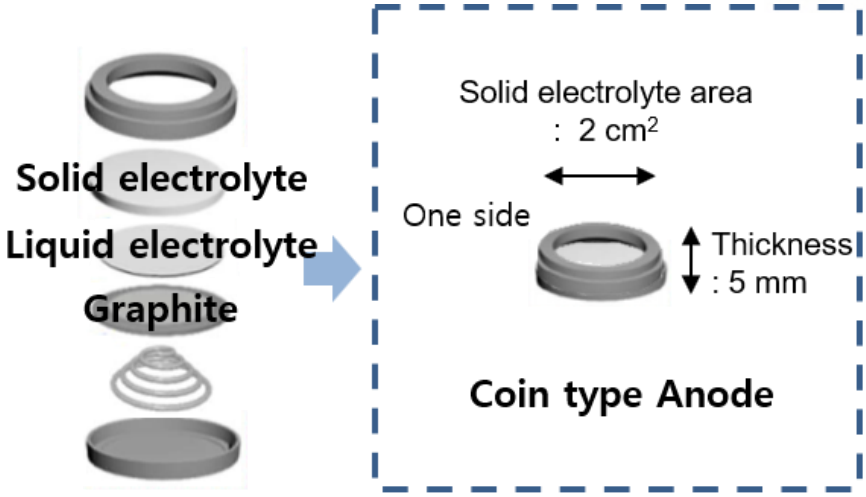
2.5.1. Need for new type WTL system

Previous research for WTL system was operated with a coin-type WTL design. However, coin-type WTL cell design has a few limits. **(Figure 37)**

First, coin-type design limits the area of a solid electrolyte. As the coin-type design is fixed and the body is metal, only 2 cm^2 of the area is possible for the lithium extraction electrochemical reaction. Due to this limited activation area, increasing the efficiency of the WTL system is limited. Also, the reaction only can happen on one side of the cell, the cathode needs to be replaced between charging and discharging. When charging and discharging, the WTL system operates at two different solutions it needs two side reactive design. Also, as the coin-type anode is thick, around 5 mm, it can have high resistance due to the thickness. In addition, the anode capacity can be limit, as the volume of the coin-type cell design is limited.

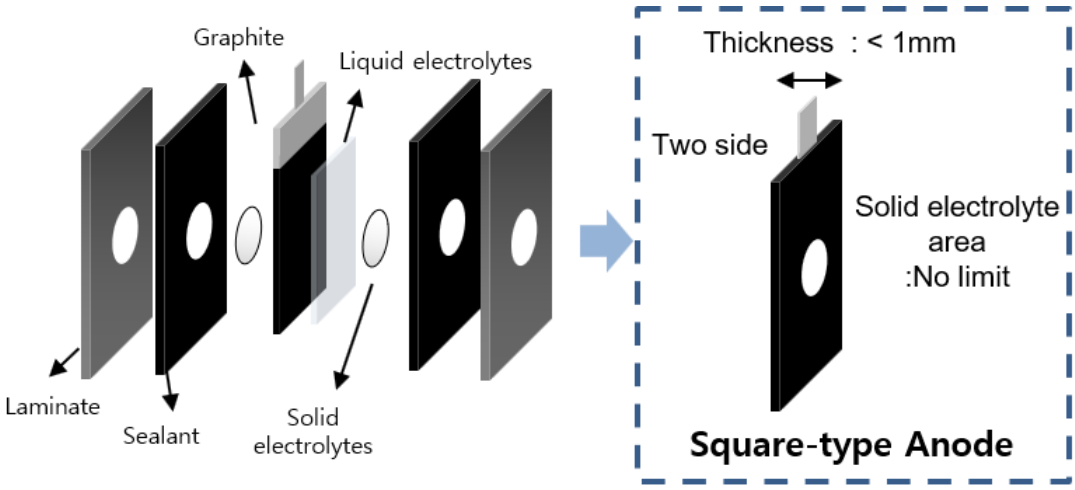
For this reason, a new-type cell design is required for the future development of the WTL system. The square-type design WTL system can be an option. **(Figure 38)** The body of the square-type design is laminate and sealant, which makes the design flexible. With this body, the area of the solid-electrolyte can be flexible and give the possibility for the large surface area of solid-electrolyte. Also, it can be designed as two sides reactive cell. With two solid electrolytes, both sides of the pouch can be used to extract lithium from waste solution and recycle lithium to Li_2CO_3. It also can be designed with a slim size, which can be lowered under 1 mm, its resistance to the contact and the entire cell system can be decreased. Also, as the design is flexible, there is no limit to the anode capacity.

With these advantages, the square-type cell was designed and fabricated. Sealant and the laminate film were used as body and the solid electrolytes were attached to the body. The graphite, which uses as an anode, was put between the body and with the heat over 200 °C, the anode body was sealed. The sealed body was fabricated with a designed plastic case, and the silicon plate to make a recycling cathode. Silicon plate was used to prevent leakage between the two cathode solutions. **(Figure 39)**



- Limit of **solid-electrolyte area** (< 2 cm^2)
- Impossible for two side reaction
- **High resistance** due to thickness (5 mm)
- **Limit of anode capacity** (< 2 cm^2)

Figure 37. Limit of the coin-type WTL cell design



- Flexible **solid-electrolyte area** (flexible cell design)
- Possible for **two side reaction**
- **Low resistance** due to slim design (< 1 mm)
- **No limit of anode capacity** (flexible cell design)

Figure 38. Square-type WTL cell design to overcome the coin-type cell design

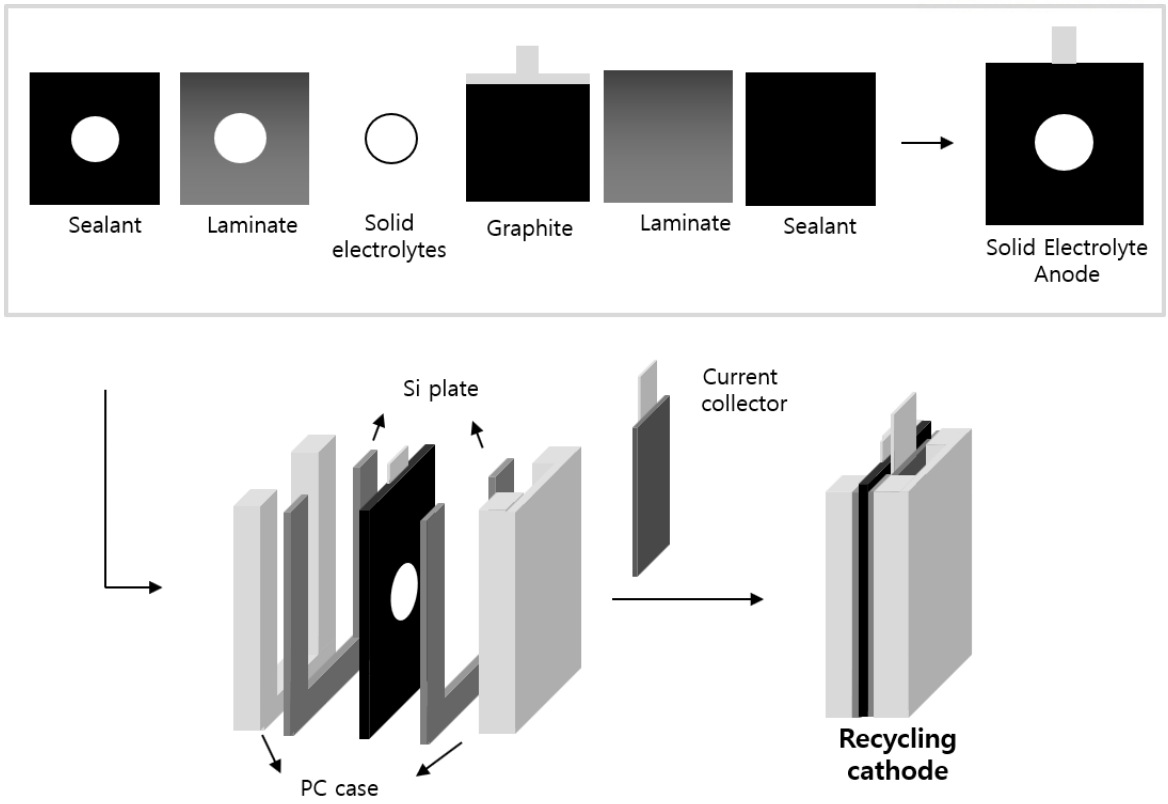


Figure 39. Square-type WTL design

2.5.2. Issue of WTL system

The mechanism and the efficiency of the WTL system were investigated with a coin-type WTL system and organized in **Table 6**. The metal recycling efficiency was 81.3 % and the energy-spent is 4×10^{-5} kWh. These efficiencies were comparable with other lithium recycling technologies. However, the main problem of the WTL system is the time spent on lithium recycling (g/h). The time spent for lithium recycling of the WTL system depends on the current density of the charging and discharging. As the time spent on lithium recycling depends on the current density of the WTL system, the WTL system needs the increasement of the current density.

For increasement of current density, the resistance must be lowered. The resistance of the WTL system affects by various components of the systems: current collector contact, the ionic conductivity of the solid electrolyte, concentration of a solution in the waste cathode compartment and active site of the electrode, etc. Among these components, cathode solution, electrode contact and the surface area of the lithium conducting solid electrolyte are possible to improve. And other components anode material, cathode solution, anode liquid electrolyte was fixed to investigate the resistance of the components. **(Figure 40)**

With the coin-type WTL system, the components were difficult to investigate, thus a new square-type WTL system was fabricated as the **figure 39**. Sealant and laminate film was fabricated at the temperature of 200°C as the body of the WTL system anode and solid electrolyte and graphite were added between the bodies. This recycling anode design was fabricated with a PC bottom and cap and between them, a silicon plate was added to completely block the liquid phase materials. These components are fixed with titanium bolts and nuts.

Table 6. Current issues for WTL system

Type	Coin-cell
Metal recycling Efficiency (%)	81.3
Energy spent (kWh)	4×10^{-5}
Time spent (g waste Li/h)	1.3×10^{-5} (Coin-cell_±0.05mA)

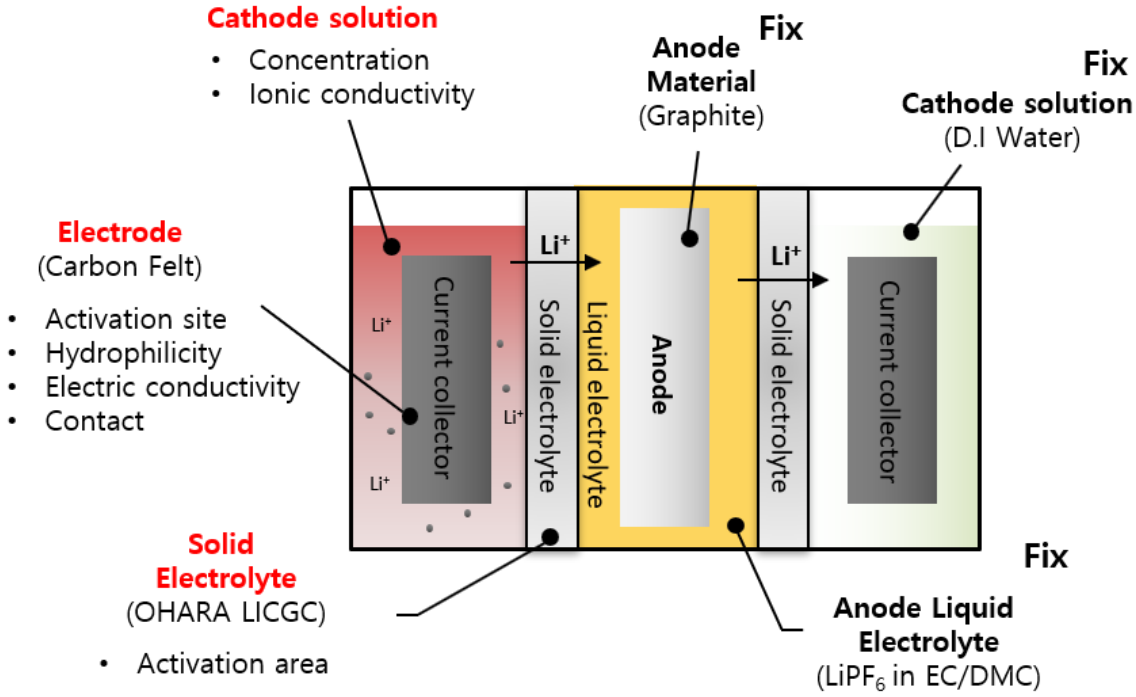


Figure 40. Component development for WTL system

2.5.3. Effect of waste cathode solution concentration on impedance of WTL system

The effect of the waste cathode solution was investigated by changing the concentration of the waste cathode solution. As lithium ions dissolve from the waste powder, the concentration of waste cathode solution depends on the waste powder amount applied at the waste cathode.

Therefore, 0.1 g, 0.2 g, 0.5 g, 1.0 g of the waste active materials are put into the waste cathode compartment of the WTL system and conductivity was investigated.

When only 0.1 g was applied in the waste cathode compartment, the conductivity of the solution showed only 1.34 mS. And as expected, the conductivity of the solution increased as the waste powder amount increases and when 1.0 g of the waste powder was applied, the conductivity showed 5.72 mS. **(Figure 41)**

With these data, the impedance of the WTL system was investigated and the Nyquist plots were shown in **figure 42**. For the WTL system, two semi-circles, each at high frequency and low frequency, was observed. As the applied waste powder amount was increased the size of the semi-circle at the low frequency decreased. This might indicate that the semi-circle at the low frequency is affected by cathodic resistance. And the high frequency semi-circle showed no change which indicates that at the high frequency, concentration does not affect.

When only 0.1 g of the waste powder was applied, cathodic resistance showed over 1200 Ω, and when the twice of the waste powder was applied, cathodic resistance decreased to almost half and it showed near 900 Ω. When 0.5 g of the waste powder was applied, cathodic resistance also decreased and applying 1.0 g of the waste powder, the resistance has decreased to near 700 Ω. With the data of impedance spectroscopy, it can be investigated that with concentration increase of the waste solution, this cathodic resistance can be decreased over 70%.

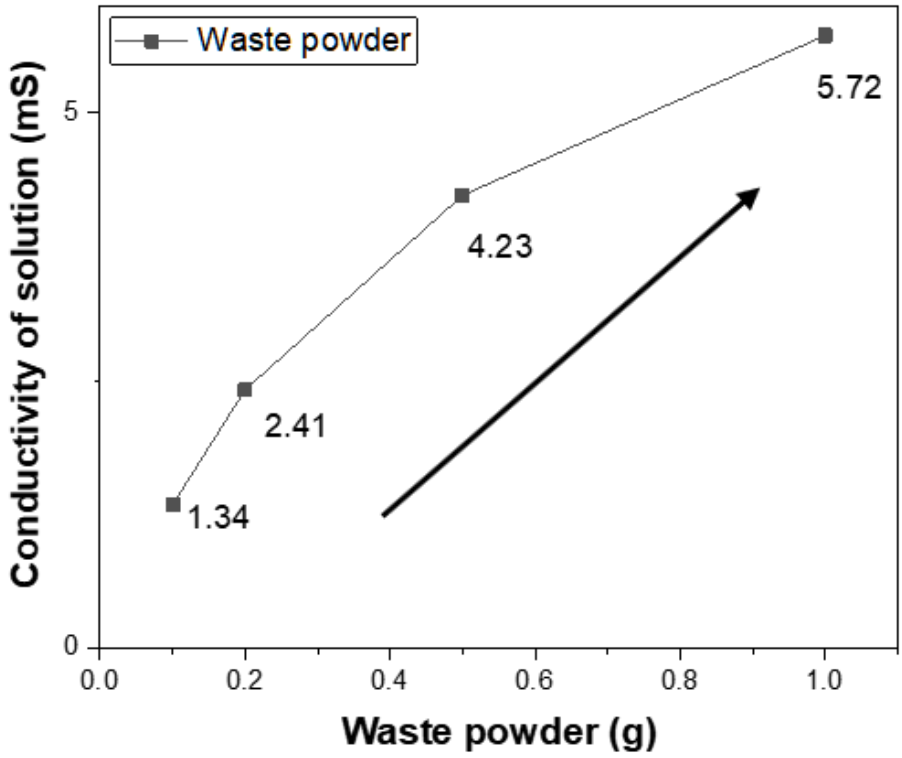


Figure 41. Ionic conductivity of waste solution toward the waste powder amount

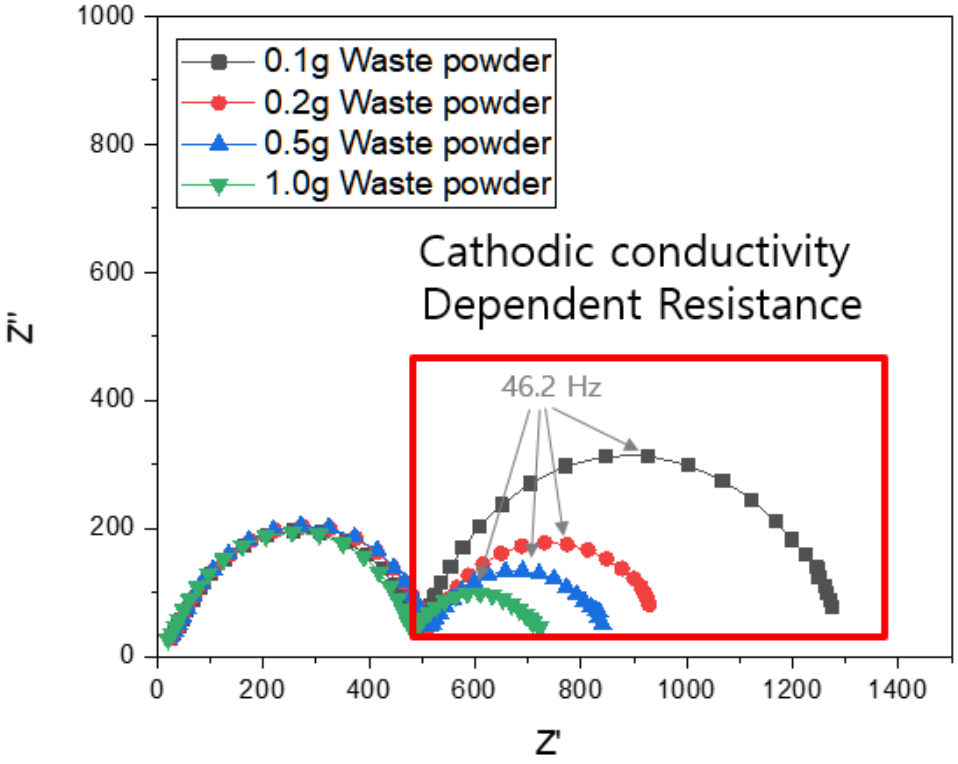


Figure 42. Effect of waste powder amount on impedance of WTL system

2.5.4. Effect of current collector contact on impedance of WTL system

The current collector of the WTL system was developed as a pouch-type electrode. The carbon felt electrode, which was used as a current collector of a coin-type WTL system, was folded and form as pouch-type, which can contain the waste powder inside the electrode. This pouch-type electrode can increase the contact of the powder and current collector, and constant contact of the powder is possible. Titanium mesh was used as a path of the electrode and fabricated with volts and nuts with carbon electrode as **figure 43**.

The effect of the contact was investigated by increasing the contact point of volt and nut. One, two and four point was contacted between carbon felt and titanium mesh and the resistance was investigated.

The resistance of the current collector electrode was measured with a multi meter and measured between the endpoint of the titanium mesh and carbon felt. When only one point of the electrode was contacted, the resistance showed 143 Ω. When the two points were contacted the resistance decreased to half. When four points were contacted, the resistance has decreased to 36 Ω which was almost 1/4 of the initial resistance.

With these data, the impedance of the WTL system was investigated and the Nyquist plots were shown in **figure 44**. As same as the Nyquist plots of the concentration change of waste cathode of a WTL system, two semi-circles, each at high frequency and low frequency, were also observed. As the contact point increases, the size of the semi-circle at the low frequency decreased. This also might indicate that the contact resistance affects the semi-circle at a low frequency. And the high frequency semi-circle also showed no change which indicates that at the high frequency, the contact of the electrode does not affect. **(Figure 45)**

In addition, the resistance was shown to be affected by the contact of the current collector and compared with the initial resistance of one contact point, when there is four contact point, the resistance was decreased to 1100 Ω which is 16% lower resistance.

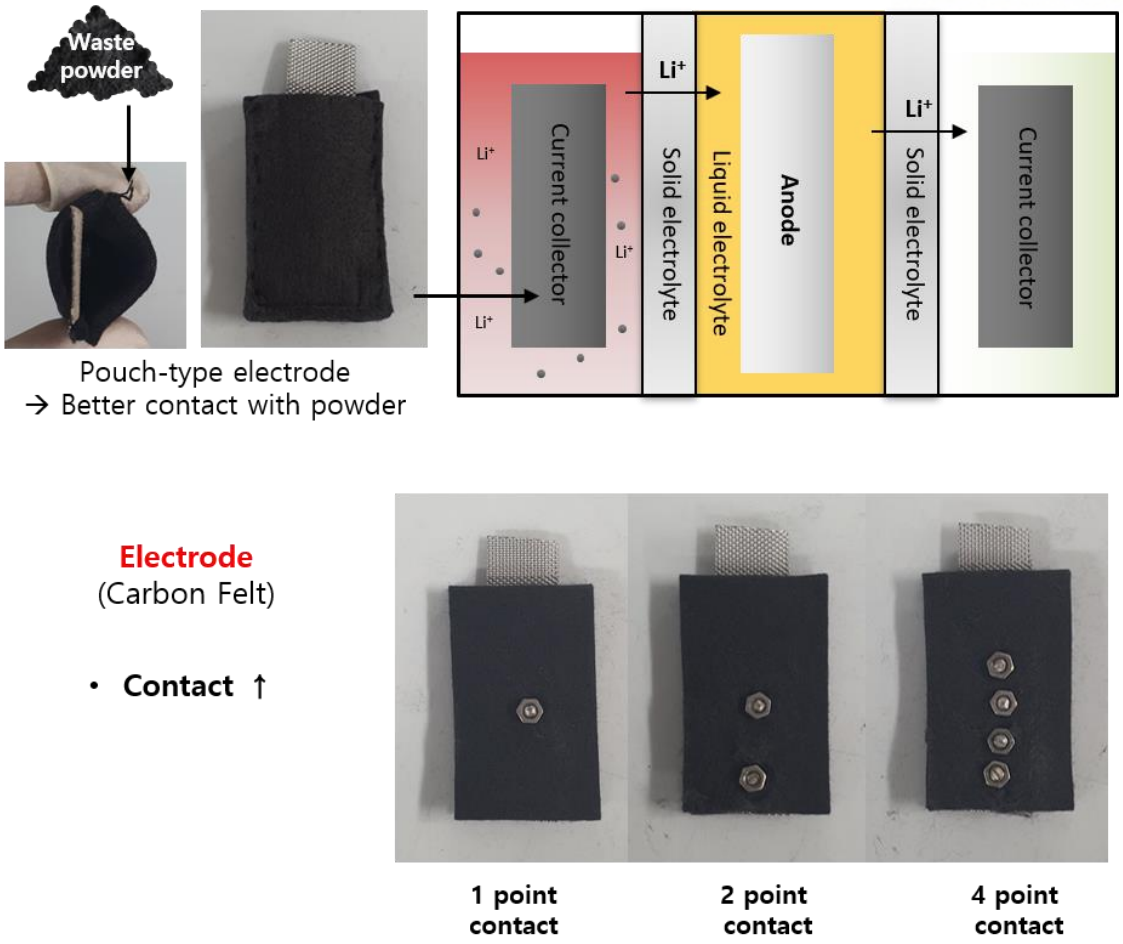


Figure 43. Pouch-type current collector electrode

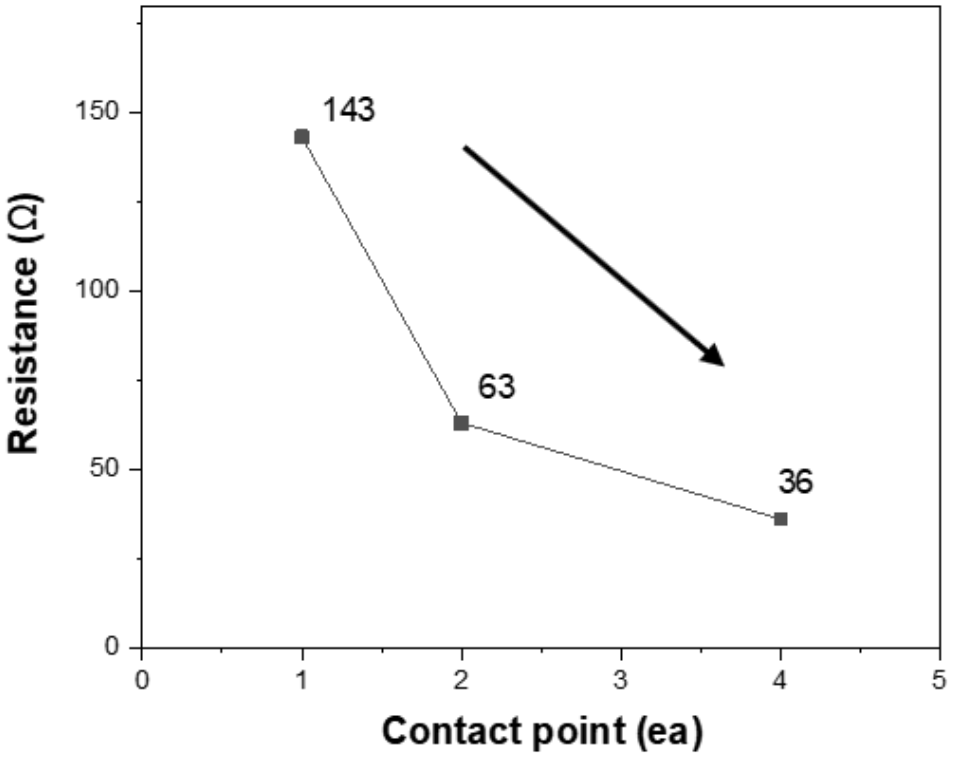


Figure 44. Effect of contact point amount on resistance of current collector electrode

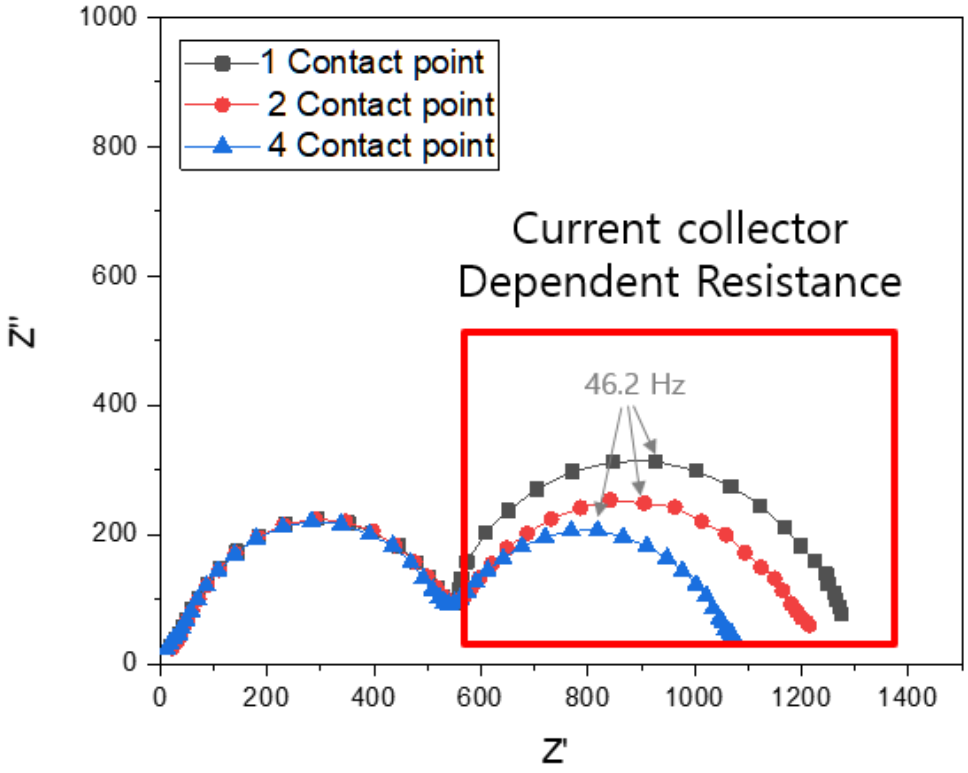


Figure 45. Effect of contact point amount on impedance of WTL system

2.5.5. Effect of solid electrolyte surface area on impedance of WTL system

The effect of solid electrolyte surface area was investigated by increasing the surface area of the LATP by adding more solid electrolytes to the WTL system. The initial solid electrolyte had an active surface area of 2 cm^3. And to compare the surface area, the WTL system that uses four solid electrolytes was fabricated and the active surface area was 8 cm^3. **(Figure 46)**

The impedance of the fabricated WTL system was investigated and the Nyquist plots were shown in **figure 47**. The large surface area WTL system showed the two semi-circles, each at high frequency and low frequency, as similar as the initial WTL system. However, the large surface area WTL system showed much lower resistance, than the initial and both semi-circles were affected by the surface area of the WTL system.

With the increasement of the surface area of solid electrolytes, low frequency semi-circle was decreased. In addition, the high frequency semi-circle also decreased as shown in **figure 47**. This indicates that increasement in the surface of the solid electrolyte can affect the overall impedance of the WTL system. Surface area increase might affect the low frequency impedance by increasing the area possible for the lithium pathway from waste lithium solution to solid electrolyte. And surface area increase affects the ionic conductivity of the solid electrolyte and increases the active area on the anodic side of the WTL system. These two factors might affect the decrease of both high frequency and low frequency semi-circle.

By comparing the resistance decrease of each factor of the WTL system, increasing the conductivity four times can decrease 43 % of the total resistance of the WTL system. And by increasing the contact point four times, it can decrease 16 % of the total resistance of the WTL system. When the surface area increased four times, 81 % of the total resistance can be decreased. These data show that among the factors of the WTL system, increasing surface area is the most effective method to decrease the total resistance. **(Figure 48)**

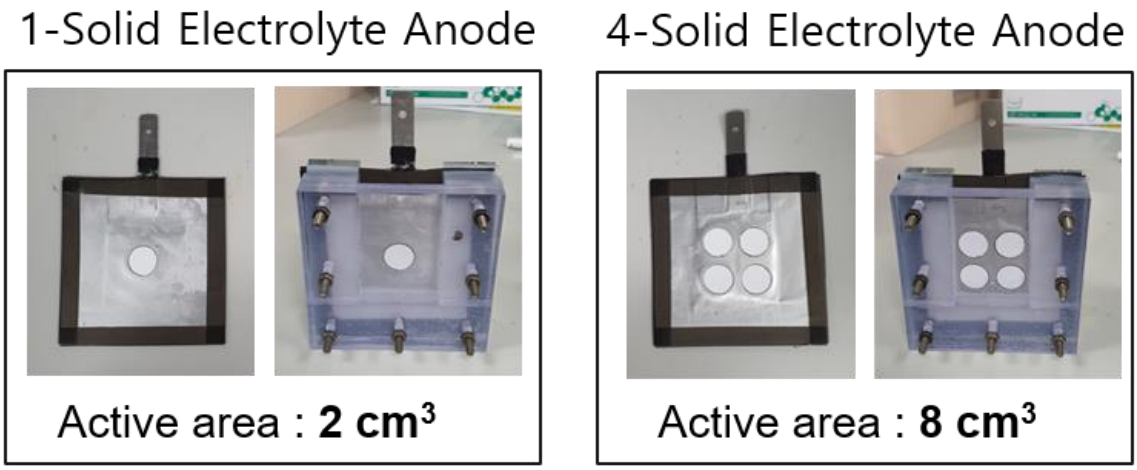


Figure 46. Increasing surface active area of WTL system

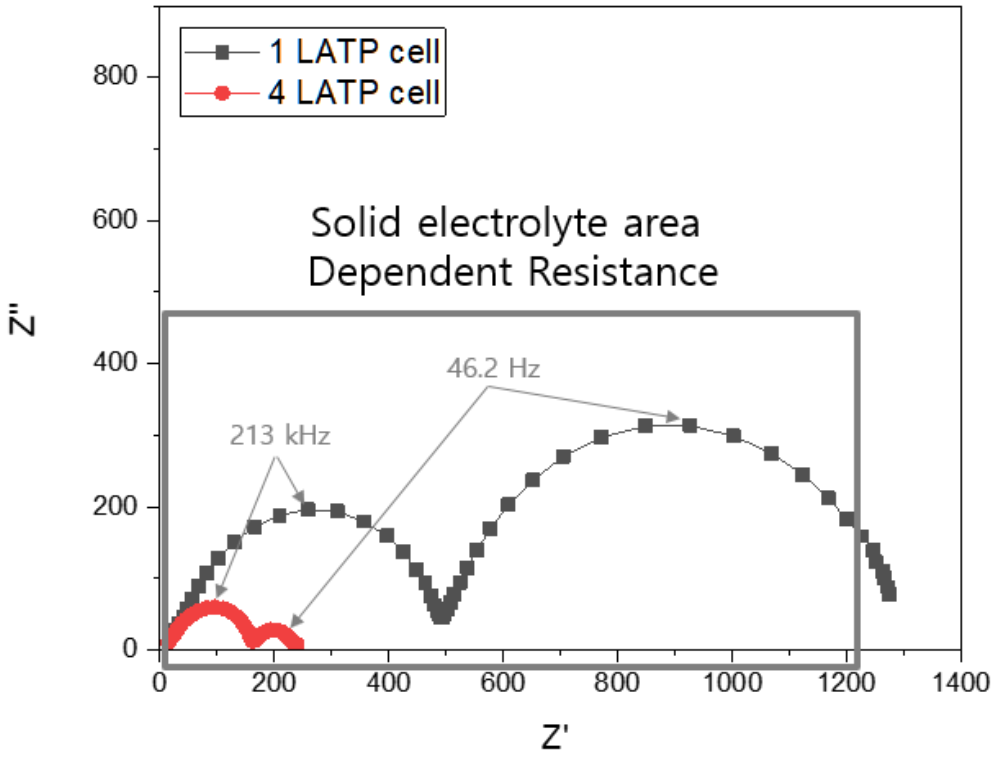


Figure 47. Effect of surface area on impedance of WTL system

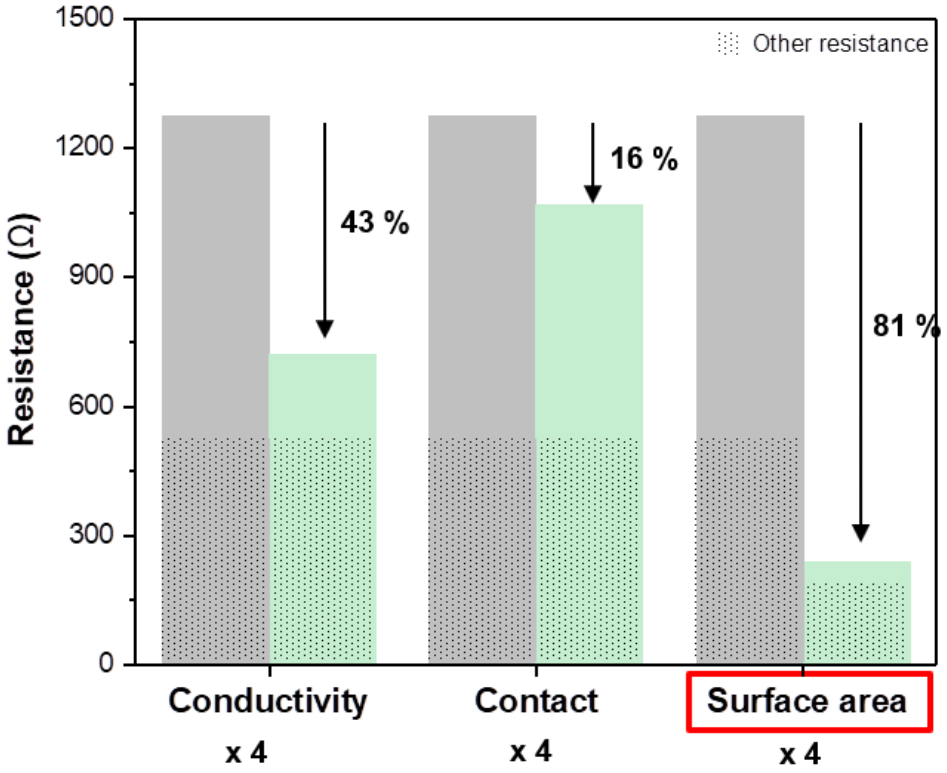


Figure 48. Effect of resistance reduction rate for each component of WTL system

2.6. Comparison of coin-type and square-type cell of WTL system

Both coin-type designed WTL system and square-type WTL system were tested to compare the efficiency and the extraction time.

First, the available current speed was investigated by increasing the current during charging. The current of the WTL for both coin and square type was increased from 0.05 mA to 1.0 mA, each current was steadily given for 5 hours. The maximum current speed of the coin-type WTL cell was 0.1 mA, which had high overpotential during the charging. However, with the square-type WTL cell, the maximum current speed was 0.5 mA. Thus, the square-type cell can operate at a 5 times higher current speed, which refers that it can extract lithium 5 times faster than the coin-type WTL cell. **(Figure 49)**

For the extraction of lithium, waste active material powders were applied to the square-type WTL system, and the charge was operated until all the available lithium ions are extracted. Compared with the coin-type WTL system, the square-type system showed a short time for the extraction of the same amount of lithium. This data shows a possibility to shorten the time of the lithium extraction with the WTL system and gives the possibility for further development of the WTL system. **(Figure 50)**

Table 7 shows the lithium recycling efficiency of square-type WTL system. It shows that the recycling efficiency of solution was 96% and the recycling efficiency of the powder was 72.3%. The recycling efficiency of the powder increased, compare with the coin-type WTL system, and this can be explained with the pouch type current collector. Pouch type current collector used for square-type WTL system has a better contact with the waste powders and is expected to lower the contact resistance of the powder with the current collector.

Table 8 shows the comparison of the coin-type cell and square-type cell of the WTL system. solid electrolyte surface area, current, metal recycling efficiency, current density, energy spent, and extraction time was compared. And as you see at the table, the constant stable current has increased as the design was developed from the coin-type WTL system. And metal recycling efficiency was slightly increased. This might come from the pouch-type current collector which has higher contact with the waste powder, followed by low contact resistance. Energy spent was calculated with charge and discharge voltage profile and showed similar energy spent with the coin-type WTL system. The most developed part after changing to square-type was extraction time, which was shortened to almost 25% compared to the coin-type system.

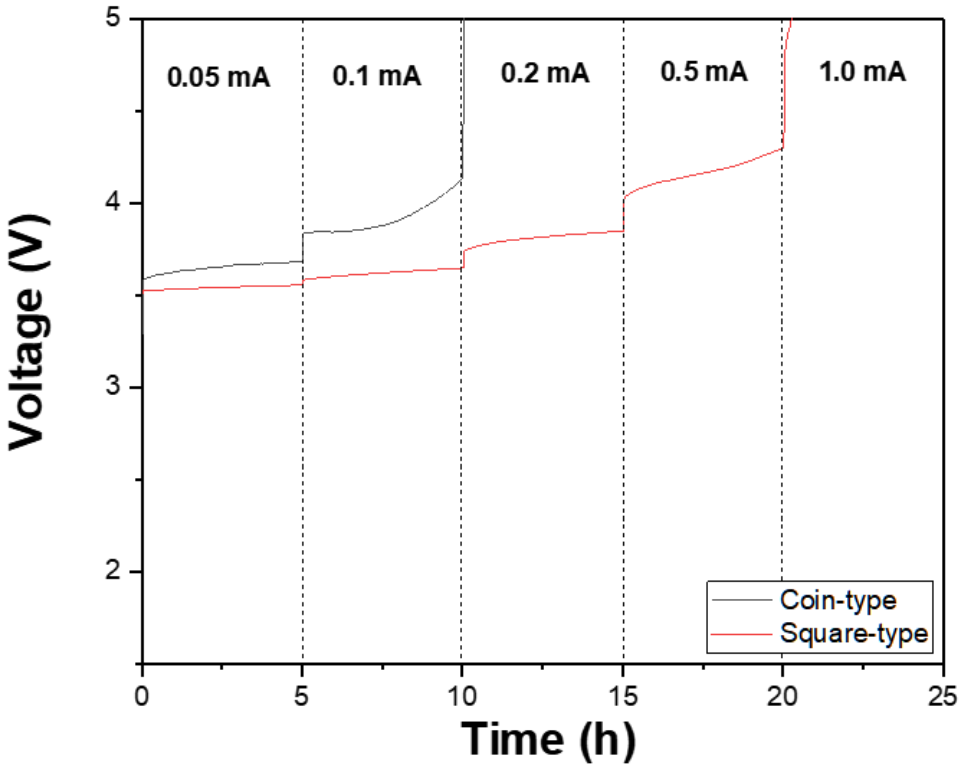


Figure 49. Effect of surface area of solid electrolyte on current rate of WTL system

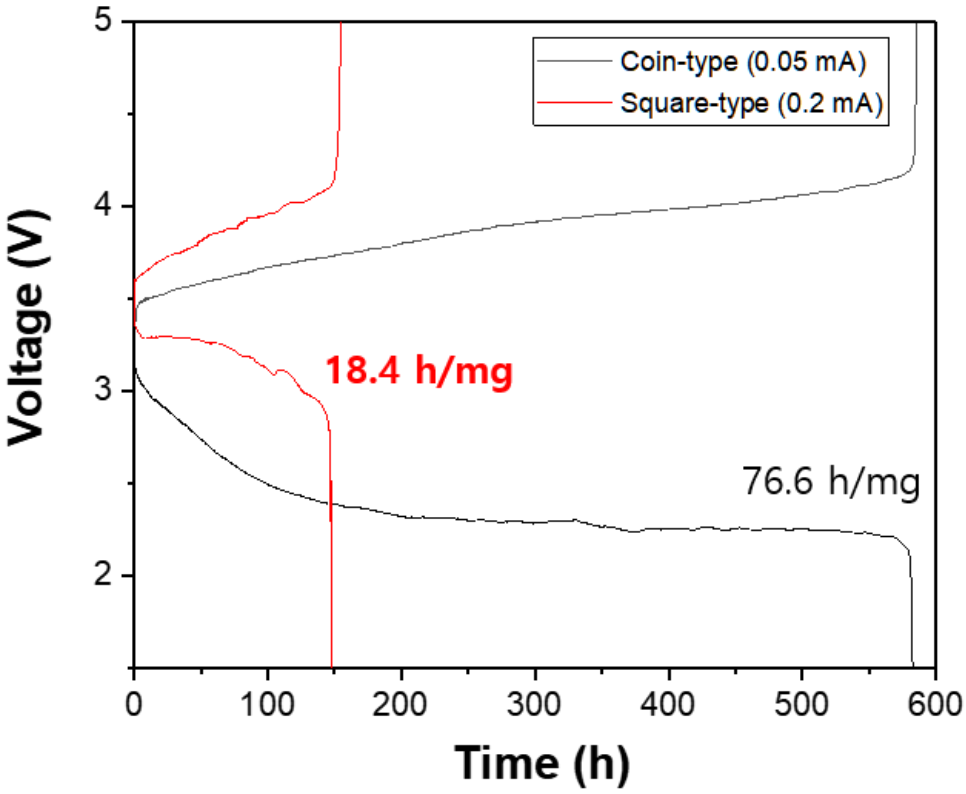


Figure 50. Charge voltage profile of square-type WTL system

Table 7. Lithium recycling efficiency of square-type WTL system

Li source	Initial Li amount (mg)	Extracted Li amount (mg)	Final Li amount (mg)
		ICP data	
Dissolved solution	5.68	5.45	0.22 **[96.0 %]**
Remain powder	3.78	2.74	1.05 [72.3 %]
Total waste powder	9.46	8.19	1.27 **[86.5%]**

Table 8. Comparison of coin-type and square-type cell for WTL system

Coin-type	**Type**	Square-type
2 cm^2	Solid electrolyte (cm^2)	8 cm^2
0.05	Current (mA)	0.2
81.3	**Metal recycling Efficiency** (%)	86.5
4 x 10^{-5}	**Energy spent** (kWh)	2.5 x 10^{-5}
76.6	Extraction time (h/mg)	18.4

2.7. Comparison with other lithium recycling system

The quantitative comparison of the WTL system and other lithium recycling systems is listed in **Table 9**. As shown in the figure, the lithium recycling rate of pyrometallurgy, precipitation, solvent extraction, selective absorption shows from 80 ~ 98 %. Comparing with the WTL system, the WTL system shows reasonable lithium recycling efficiency.

In addition, the other methods require additional chemical costs to extract lithium from waste lithium-ion batteries. However, the WTL system only uses water to extract the lithium from the lithium-ion batteries, which does not cost any chemical cost.

Also, for pyrometallurgy, high temperature is required to react the lithium-ion battery materials to dissolve the lithium into water. And for hydrometallurgy, a temperature over 50 °C is required to dissolve the waste lithium-ion battery powders into acids or bases. However, the WTL system operates at room temperature, which does not require a high energy temperature rise.

Finally, both pyrometallurgy and hydrometallurgy have potential pollutions after the lithium recycling treatment, such as volatile organic compounds or acidic wastes. However, the WTL system is an eco-friendly system, that has no pollution. This can be explained that WTL only uses water and other chemical wastes are not created during charging and discharging.

Table 9. Comparison with other lithium recycling technologies

Method	Recycle Efficiency (%)	Additional Chemical Cost ($/kg)	Temperature (℃)	Potential pollutions
Hydrometallurgy [Precipitation]	82 ~ 98.2	37.46 (CH_2O_2, H_2O_2 Etc.)	50-100	Inorganic waste Acidic waste
Hydrometallurgy [Solvent extraction]	Leaching efficiency ≈100	80.12 (H_2SO_4, PC88A Etc.)	50-100	Inorganic waste organic waste Acidic waste
Hydrometallurgy [Selective adsorption]	Leaching efficiency 81.2	111 (NH_3, HCl Etc.)	60-90	Acidic waste
WTL system	**86.5** (86.8)	**D.I water**	**25** (Room temp.)	**No pollution**

3. Experimental

3.1. Preparation WTL system components

19 mm diameter and 0.8 mm thickness lithium ion conducting glass ceramic (LICGC), $Li_{1+x+3z}Al_x(Ti,Ge)_{2-x}Si_{3z}P_{3-z}O_{12}$, were purchased from OHARA Inc.(Japan) The ionic conductivity of the LICGC was measured to be 10^{-4} S/cm at room temperature. An organic liquid electrolyte, 1 M $LiPF_6$ in ethylene (EC-DMC) (1:1 volume %), was purchased from Panaxetec Corp. (99.9 %, Korea) A 25 μm thickness polyethylene(PE) separator was purchased from Celgard. (Korea)Graphite used for anode was purchased in Sigma-Aldrich. (99 %, Korea) The graphite powder was mixed with a carbon black conducting agent (TIMCAL Super P) and a polyvinylidenedifluoride(PVDF) binder at a weight ratio of 90:5:5 in N- Methyl-2-pyrrolidone(NMP), and cast on copper foil and dried in an oven at 80°C. Carbon felt of electrical resistivity less than 20 Ω -mm was purchased in Dissol and used as the current collector.

3.2. Preparation coin-type WTL system

The coin-type WTL system was fabricated with a cap and bottom of the coin cell. At the cap of the coin cell, a solid electrolyte is completely attached, and inside the coin cell, spring, separator, graphite anode and drop of liquid electrolyte are applied in the argon filled glove box. And the top of the coin cell was sealed to the top to make harvesting anode. This harvesting anode was fabricated with a carbon felt current collector, cathode cap and bottom, to make a coin-type WTL cell.

3.3. Preparation square-type WTL system

The square-type WTL system was fabricated with laminate film and sealant. On the laminate and sealant, solid electrolytes are completely attached, between the laminate and sealant, separator, graphite anode and liquid electrolyte are applied in the argon filled glove box. And laminate and sealant are heated to 200 °C to attach the sealant and seal the anode compartment completely.

This square-type harvesting anode was fabricated with a PC case and silicon plate to make a sealed container of the waste cathode. The PC case and the silicon plate are fabricated with titanium volt and nut and fabricated to make a square-type WTL cell.

3.4. Characterizations

The X-ray diffraction (XRD) was obtained with an X-ray diffractometer (D8 ADVANCE, Bruker AXS, Korea). Rietveld refinement was carried out in the 2θ range = 10-80°, with a 0.5° step interval and a 10 s step time. The Inductively Coupled Plasma -Mass Spectrometry (ICP-MS) measurement

was performed by 700-ES from Varian Inc. (Korea) The electrochemical tests were performed by a Galvanostatic charge-discharge unit (WonATech. Co., Korea)

4. Conclusion

The age of battery of things (BoT) is approaching as energy is the most important source for the future. Among the batteries, lithium-ion batteries are the promising and most using secondary battery, which has long cycle ability, and high energy density and has low self-discharge rate. These lithium-ion batteries have been used in portable electronics, such as cell phones or laptops, and are applied to high energy-requiring applications such as energy storage systems and electric vehicles.

However, lithium-ion battery is meeting challenges of material supply. The most essential element of the lithium-ion battery is lithium, which directly involves at the electric reaction of the lithium-ion battery. This lithium is a limited source on the earth, and some researchers are concerned about lithium depletion in few decades.

For this reason, the WTL system was developed to recycle lithium from the waste lithium-ion batteries to form Li_2CO_3. This system only uses water to extract lithium with electrochemical reactions during the charging and discharging of the system.

The WTL system was designed with a solid electrolyte and carbon current collector, and the mechanism was investigated with pH and potential transition and ICP. During charging and discharging OER/ ORR are expected to occur at the solution to extract lithium from waste active materials and a delithiation reaction of the cathode material is expected to occur from the waste powders. From the WTL system, the total lithium recycling efficiency was 81.3 % and the energy consumption for lithium recycling was 0.06 kWh, However, the drying energy can be ignored when the continuous discharge occurs with ORR and the water elimination occurs.

To improve the characteristics of the WTL system, each component is investigated with impedance by developing a square-type cell. The methods to improve the efficiencies of the WTL system are investigated. The square-type cell was then compared with the coin-type cell and time spent was decreased more than 4 times.

This newly developed WTL lithium recycling system has fine lithium recycling efficiency, and no additional chemical cost is needed to operate the system. Also, it operates at room temperature which leads it to the low energy recycling technology. In addition, it is an eco-friendly lithium-recycling system that has no potential pollutions during lithium recycling. However, for the future commercialize of the system, it requires further research. As mentioned above, the current speed of

the systems needs more development and for the current speed, increasing the surface area of the solid electrolyte was the most effective method for the WTL system. However, to increase the solid electrolyte surface WTL system requires a lot of solid electrolytes, and the problem is that the solid electrolyte price too high ($300 for 2cm^2 solid electrolyte) for the current purchase state. For the commercialization, the system price will be near $800,000 with the current solid electrolyte price, which is the same price of recycling 100 tons of waste lithium-ion battery materials with the hydrometallurgy method. Although once the WTL is constructed, it has the advantage that there is no additional chemical cost for lithium recycling, the system price is too high for the current state. Therefore, lowering the price of the lithium-ion conducting solid electrolyte is essential for commercialization, and if the price of the solid electrolyte is below $5 per 2cm^2, this system might be considered for commercialization. Although it needs further research for commercialization, the WTL system is a promising lithium recycling technology for the sustainable future energy market since it has a strong advantage of operating at room temperature and is environmentally friendly.

REFERENCES

[1] M. Garside, Total global consumption of lithium from 2008 to 2016, 2019

[2] Sociedad Química y Minera de Chile S.A., Annual Report 2019, 2020

[3] M. Garside, Total global consumption of lithium from 2008 to 2016, 2019

[4] Hanna Vikström, Simon Davidsson and Mikael Höök, Applied Energy, 2013, 110, 252

[5] M. Garside, Distribution of lithium end-usage worldwide in 2019, by area of application, 2020, https://www.statista.com/statistics/268787/lithium-usage-in-the-world-market/

[6] Gruber and Paul W., Journal of Industrial Ecology, 2011, 15, 5, 760

[7] TALISON LITHIUM, Lithium, https://www.talisonlithium.com/lithium

[8] Totten, George E.; Westbrook, Steven R. and Shah, Rajesh J., ASTM International, 2003, 559

[9] Lu, Y. Q., Zhang, G. D., Jiang, M. F., Liu, H. X. and Li, T. Materials Science Forum, 2011, 675: 877

[10] Bansal, Raj K., 1996, 192, ISBN 978-0-7637-0665-4

[11] P.Meshram, B.D. Pandey and T.R. Mankhand, Hydrometallurgy, 2014, 150, 192

[12] Gui Liu, Zhongwei Zhao and Ahmad Ghahreman, Hydrometallurgy, 2019, 187, 81

[13] Labbé, J.F. and Daw, G. Panorama 2011 du marché du lithium; Rapport public 2012, BRGM/RP-61340-FR; BRGM: Orléans, France, 2012

[14] Steve H. Mohr,, Gavin M. Mudd and Damien Giurco, Minerals 2012, 2, 65

[15] Garrett, D.E., Handbook of Lithium and Natural Calcium Chloride: Their Deposits, Processing, Uses and Properties, 1st ed.; Elsevier, 2004

[16] Andrés Yaksic and John E.Tilton, Resources Policy, 2009, 34, 185

[17] Peng Chen, Siyang Tang, Hairong Yue, Changjun Liu, Chun Li, and Bin Liang, Industrial & Engineering Chemistry Research, 2017, 56, 5668

[18] Bauman, W. C. and Burba, J. L., Composition for the recovery of lithium values from brine and 373 process of making/using said composition. Google Patents, 2001

[19] Xuheng Liu, Maoli Zhong, Xingyu Chen and Zhongwei Zhao, Hydrometallurgy, 2018, 176, 73

[20] Saltworks, Lithium Brine Extraction Technologies & Approaches, June 8th, 2018, https://www.saltworkstech.com/articles/lithium-brine-extraction-technologies-and-approaches/ (accessed on xx.xx 2021)

[21] Roskill Information Services Ltd., "The Economics of Lithium", Eleventh Edition, 2009

[22] Ye Zhang, Yuehua Hu, Li Wang and Wei Sun, , Minerals Engineering, 2019, 139, 105868

[23] Kyle Pennell, How Does Lithium Mining Work?, 2018, https://blog.grabcad.com/blog/2018/02/20/how-does-lithium-mining-work/

[24] Victoria Flexer, Celso Fernando Baspineiro and Claudia Inés Galli, Science of the Total Environment, 2018, 639, 1188

[25] Robert F. Service, Seawater could provide nearly unlimited amounts of critical battery material, Science, 2020

[26] M. Garside, Average lithium carbonate price from 2010 to 2019 (in U.S. dollars per metric ton), 2020, https://www.statista.com/statistics/606350/battery-grade-lithium-carbonate-price/

[27] Lithium-Ion Battery Market by Type, Power Capacity, Industry, Voltage, Region-Global Forecast to 2025, 2020

[28] Yuanli Ding, Zachary P. Cano, Aiping Yu, Jun Lu and Zhongwei Chen, Electrochemical Energy Reviews, 2019, 2, 1

[29] How much Lithium is in a Li-Ion Vehicle Battery, 2017, https://www.linkedin.com/pulse/how-much-lithium-li-ion-vehicle-battery-paul-martin/

[30] U.S. Geological Survey, Mineral Commodity Summaries, January 2020

[31] Altura Lithium: New Significant Supply to the Battery market in 2018, 2018, page 26

[32] Projection of total worldwide lithium demand from 2018 to 2025 (in 1,000 metric tons of lithium carbonate equivalent), 2019

[33] Dana L. Thompson, Jennifer M. Hartley, Simon M. Lambert, Muez Shiref, Gavin D. J. Harper, Emma Kendrick, Paul Anderson, Karl S. Ryder, Linda Gaines and Andrew P. Abbott, Green Chem., 2020, 22, 7585

[34] Liang An, Recycling of Spent Lithium-Ion Batteries, Processing Methods and Environmental Impacts, 2019

[35] Mitch Jacoby, Chemical & Engineering, (2019) 97, Issue 28, https://cen.acs.org/materials/energy-storage/time-serious-recycling-lithium/97/i28,

[36] C. Pillot, presented at the 31st International Battery Seminar & Exhibit, Fort Lauderdale, FL, USA, 2017

[37] Daniel Hauck and Michael Kurrat, Overdischarging Lithium-Ion Batteries, Springer, 2018

[38] Arno Kwade and Jan Diekmann, Recycling of Lithium-Ion Batteries; The LithoRec Way, Sustainable Production, Life Cycle Engineering and Management, 2018, Chapter 4, 53

[39] James Shaw-Stewart, Anna Alvarez-Reguera, Agata Greszta, James Marco, Maryam Masood, Rob Sommerville and Emma Kendrick, Sustainable Materials and Technologies, 2019, 22, e00110

[40] Tao Zhang, Yaqun He , Fangfang Wang , Linhan Ge , Xiangnan Zhu and Hong Li, Waste Management, 2014, 34, 1051

[41] Daniel A. Bertuol, Camila Toniasso, Bernardo M. Jimenez, Lucas Meili, Guilherme L. Dotto, Eduardo H. Tanabe and Monica L. Aguiar, Journal of Power Sources, 2015, 275, 62

[42] Francesca Pagnanelli , Emanuela Moscardini, Pietro Altimari, Thomas Abo Atia and Luigi Toro, Waste Management, 2016, 51, 214

[43] XueWang, GabrielleGaustad and Callie W.Babbitt, Waste Management , 2016, 51, 204

[44] Francesca Pagnanelli, Emanuela Moscardini, Pietro Altimari, Thomas Abo Atia and Luigi Toro, Waste Management, 2017, 60, 706

[45] Yu Zhang, Yaqun He, Tao Zhang, Xiangnan Zhu, Yi Feng, Guangwen Zhang and Xuejie Bai, Journal of Cleaner Production, 2018, 202, 736

[46] Li Li , Jing Ge , Renjie Chena, Feng Wua,, Shi Chen and Xiaoxiao Zhang, Waste Management, 2010, 30, 2615

[47] Xiangping Chen and Tao Zhou, Waste Management & Research, 2014, 32, 11, 1083

[48] Li-Po He, Shu-Ying Sun, Xing-Fu Song and Jian-Guo Yu, Waste Management, 2015, 46, 523

[49] Xiangping Chen, Chuanbao Luo, Jinxia Zhang, Jiangrong Kong, and Tao Zhou, ACS Sustainable Chemistry & Engineering, 2015, 3, 3104

[50] Liang Sun and Keqiang Qiu, Waste Management, 2012, 32, 1575

[51] Pratima Meshram, B.D. Pandey and T.R. Mankhand, Chemical Engineering Journal, 2015, 281, 418

[52] Christian Hanisch, Thomas Loellhoeffel, Jan Diekmann, Kely Jo Markley, Wolfgang Haselrieder and Arno Kwade, Journal of Cleaner Production, 2015, 108, 301

[53] Yue Yang, Guoyong Huang, Shengming Xu, Yinghe He and Xin Liu, Hydrometallurgy, 2016, 165, 390

[54] S. Aktas, D. J. Fray, O. Burheim, J. Fenstad and E. Açma, Metallurgy, 2006, 115, 2, 95

[55] Jessica Frontino Paulino, Nat ´ alia Giovanini Busnardo and Julio Carlos Afonso, Journal of Hazardous Materials, 2008, 150, 843

[56] Rong-Chi Wang, Yu-Chuan Lin and She-Huang Wu, Hydrometallurgy, 2009, 99, 194

[57] ZHU Shu-guang, HE Wen-zhi, LI Guang-ming, ZHOU Xu, ZHANG Xiao-jun and HUANG Ju-wen, Transactions of Nonferrous Metals Society of China, 2012, 22, 2274

[58] Haiyang Zou, Eric Gratz, Diran Apelian and Yan Wang, Green Chem., 2013, 15, 1183

[59] Xihua Zhang, Hongbin Cao, Yongbing Xie, Pengge Ning, Huijiao An, Haixia You and Faheem Nawaz, Separation and Purification Technology, 2015, 150, 186

[60] Xiangping Chen, Tao Zhou, Jiangrong Kong, Huaxiong Fang and Yongbin Chen, Separation and Purification Technology, 2015, 141, 76

[61] Wenfang Gao, Xihua Zhang, Xiaohong Zheng, Xiao Lin, Hongbin Cao, Yi Zhang, and Zhi Sun, Environmental Science & Technology, 2017, 51, 1662

[62] Yongxia Yang, Xiaohong Zheng, Hongbin Cao, Chunlong Zhao, Xiao Lin, Pengge Ning, Yi Zhang, Wei Jin, and Zhi Sun, ACS Sustainable Chemistry & Engineering, 2017, 5, 9972

[63] Subramanian Natarajan, Arvind B. Boricha and Hari C. Bajaj, Waste Management, 2018, 77, 455

[64] Yongxia Yang, Xiangqi Meng, Hongbin Cao, Xiao Lin, Chenming Liu, Yong Sun,d Yi Zhang and Zhi Sun, Green Chem., 2018, 20, 3121

[65] Wenfang Gao, Jiali Song, Hongbin Cao, Xiao Lin, Xihua Zhang, Xiaohong Zheng, Yi Zhang and Zhi Sun, Journal of Cleaner Production, 2018, 178, 833

[66] Shengdong Tao, Jian Li, Lihua Wang & Leshan Hu and Hongming Zhou, Ionics, 2019, 25, 5643

[67] Rabia Sattar, Sadia Ilyas, Haq Nawaz Bhatti and Abdul Ghaffar, Separation and Purification Technology, 2019, 209, 725

[68] Yue Yang , Shaole Song , Shuya Lei , Wei Sun , Hongshuai Hou , Feng Jiang a, Xiaobo Ji, Wenqing Zhao and Yuehua Hu, Waste Management, 2019, 85, 529

[69] Quan Li, Ka Yip Fung, Lingda Xu, Christianto Wibowo, and Ka Ming Ng, Industrial & Engineering Chemistry Research, 2019, 58, 3118

[70] Li Li, Yifan Bian, Xiaoxiao Zhang, Ying Yao, Qing Xue, Ersha Fan, Feng Wu and Renjie Chen, Waste Management, 2019, 85, 437

[71] Chang-Heum Jo and Seung-Taek Myung, Journal of Power Sources, 2019, 426, 259

[72] Prasad Yadav, Chan Jun Jie, Shermaine Tan and Madhavi Srinivasan, Journal of Hazardous Materials, 2020, 399, 123068

[73] Weiguang Lv, Zhonghang Wang, Xiaohong Zheng, Hongbin Cao, Mingming He, Yi Zhang, Haijun Yu, and Zhi Sun, ACS Sustainable Chemistry & Engineering, 2020, 8, 13, 5165

[74] Yingchao Zhang, Wenqiang Wang, Jiehui Hu, Tao Zhang, and Shengming Xu, ACS Sustainable Chemistry & Engineering, 2020, 8, 15496

[75] Pingwei Zhang, Toshiro Yokoyama, Osamu Itabashi, Toshishige M. Suzuki and Katsutoshi Inoue, Hydrometallurgy, 1998, 47, 259

[76] Giuseppe Granata, Emanuela Moscardini, Francesca Pagnanelli, Franco Trabucco and Luigi Toro, Journal of Power Sources, 2012, 206, 393

[77] Wei-Sheng Chen and Hsing-Jung Ho, Metals, 2018, 8, 321

[78] Thomas Abo Atia, Giuseppe Elia, Robert Hahn, Pietro Altimari and Francesca Pagnanelli, Journal of Energy Chemistry, 2019, 35, 220

[79] Lei Xu, Chen Chen and Ming-Lai Fu, Hydrometallurgy, 2020, 197, 105439

[80] Hongyan Wang, Kai Huang, Yang Zhang, Xin Chen, Wei Jin, Shili Zheng, Yi Zhang and Ping Li, , ACS Sustainable Chemistry & Engineering, 2017, 5, 11489

[81] T. Georgi-Maschler, B. Friedricha, R. Weyhe, H. Heegn and M. Rutz, Journal of Power Sources, 2012, 207, 173

[82] Jia Li, Guangxu Wang and Zhenming Xu, Journal of Hazardous Materials, 2016, 302, 97

[83] Jiefeng Xiao, Jia Li, and Zhenming Xu, Environmental Science & Technology, 2017, 51, 11960

[84] Jiefeng Xiao, Jia Li and Zhengming Xu, Journal of Hazardous Materials, 2017, 338, 124

[85] Juntao Hu, Jialiang Zhang, Hongxu Li, Yongqiang Chen and Chengyan Wang, Journal of Power Sources, 2017, 351, 192

[86] Hui Dang, Benfeng Wang, Zhidong Chang, Xue Wu, Jingge Feng, Hualei Zhou, Wenjun Li, and Changyan Sun,ACS Sustainable Chemistry & Engineering, 2018, 6, 13160

[87] Sanjay Pindar and Nikhil Dhawan, Journal of Operations Management, 2019, Vol. 71, No. 12

[88] Chao Pengb, Fupeng Liu, Zulin Wang, Benjamin P. Wilson and Mari Lundström, Journal of Power Sources, 2019, 415, 179

[89] Samane Maroufi , Mohammad Assefi, Rasoul Khayyam Nekouei and Veena Sahajwalla, Sustainable Materials and Technologies, 2020, 23, e00139

[90] Sanjay Pindar and Nikhil Dhawan, Journal of Thermal Analysis and Calorimetry, 2020, https://doi.org/10.1007/s10973-020-10139-6

[91] Nina Mahootcheian Asl, Seong Shen Cheah, Jason Salim and Youngsik Kim, RSC Advances, 2012, 2, 6094

[92] Ananth Govind Rajan, Emily A. Carter, Energy Environ. Sci., 2020, 13, 4962-4976

ACKNOWLEDGEMENT

가장 먼저 부족한 저에게 좋은 기회를 주시고, 6년 넘게 가르침을 주신 김영식 지도 교수님께 진심 어린 감사를 드립니다. 교수님께 학문적인 분야 뿐 만 아니라, 인생을 배울 수 있었습니다. 교수님의 가르침을 따라 앞으로 박사로써 전문적이며, 주도적인 연구자가 되어, YK group에 도움이 되는 연구자가 되겠습니다.

또한 정말 가족 같은 우리 YK group member들에게 정말 감사합니다. 지식 창고가 되어 주었던 영진이형, 연구자로써 배울 구석이 많은 우석이, 미국에서 열심히 하는 제희, 연구할 때만은 진지해지는 진호형, 친동생 같은 영재, YK의 참된 일꾼 남혁이, 걸크러시 동생 세영이, 굳은 일도 도맡아 하는 착한 도완이, 많이 변한 착한 준호, 잘생기고 키 큰 종우, 부산 친구 성우, 조용하게 똑똑한 지훈이, 귀염뽀짝 서해, 너무 너무 성실한 광호, 항상 바쁜 동엽이, 조용하게 재밌는 정우, YK와 인연인 왕근이형, 친절히 대해 주셨던 Ahmad 박사님 내외, 그리고 정말 의지가 많이 되었던, 졸업하신 정선, 진협, 용일, 현우, 영준 선배님들… 이 group과 함께 하였기에, 끝까지 재미있게 연구를 할 수 있었습니다. 정말 감사합니다.

그리고 저희 그 외 연구적으로 많은 도움을 주신, 서인석 교수님, 왕제필 교수님, 황수민 박사님, 신선명 박사님도 감사합니다.

부족한 저에게 아끼는 딸을 허락해주신 장인어른, 장모님께 감사를 드리며, 저를 바르게 키워 주시고, 연구자로써의 길을 응원해주신 사랑하는 어머니, 아버지께 감사드립니다. 미국에 있는 동생 진환이, 외할머니, 친할머니, 할아버지께도 감사의 말씀을 전합니다. 가족이란 든든한 버팀목이 있었기에 앞으로 나아갈 수 있었습니다.

마지막으로, 제 인생의 1/3을 저를 믿고 사랑해준, 사랑하는 아내 초희와 초희가 준 선물인 우리 지우에게 사랑을 담아 고마움을 전합니다.